CHARACTERISATION OF SOLID RESIDUES FROM COAL LIQUEFACTION PROCESSES

Final Report

by

Energy Research Unit,
University of Regina

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada

DSS FILE NUMBER	:	01ST.23440-2-9102
DSS CONTRACT SERIAL NUMBER	:	OST 82-00067
CANMET PROJECT NUMBER	:	430601
CANMET SCIENTIFIC AUTHORITY	:	Dr. J. Price

DATE: June, 1983

MICROMEDIA
DEC 22 1983

This report should be cited as Contract Report No: OST 82-00067

144 pp

Energy Research Unit

Contribution #55

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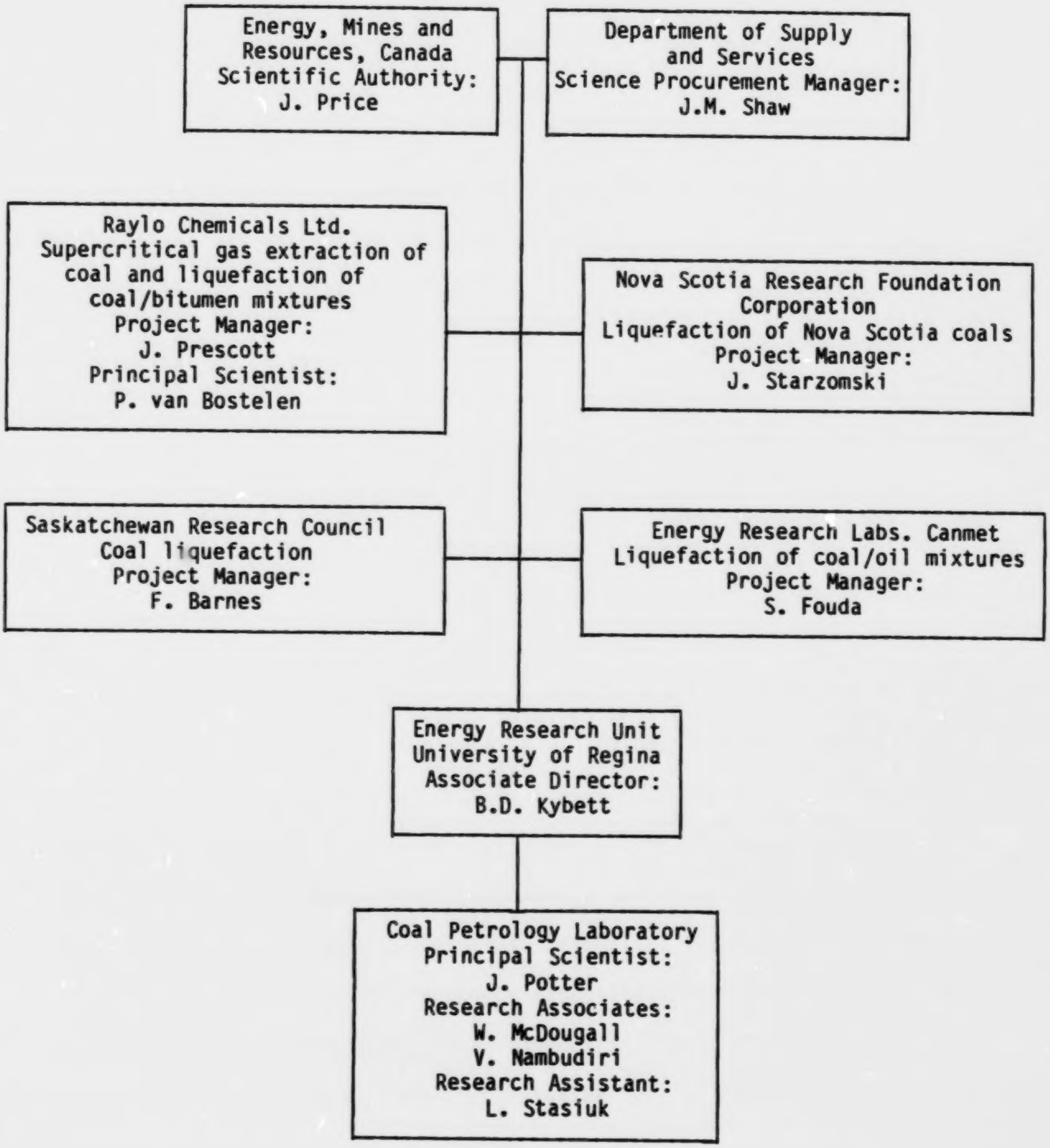

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EXECUTIVE SUMMARY

Coal feedstocks and solid products from coal liquefaction and coal-bitumen coprocessing experiments conducted by four Canmet-sponsored research groups are studied using petrographic methods supplemented by trace element data obtained by SEM-EDS. Maceral analyses and reflectance data are used to assess the petrographic compositions and ranks of the coal feedstocks. The contents of reactor samples, solid products and distillation residues from various coal liquefaction processes are classified according to the optical characters of the microscopical components. The origins of the residue components are identified petrographically and by trace element studies of petrographically selected components.

Raylo Chemicals Ltd. conducted two sets of experiments from which the coals feedstocks and solid products are examined. Firstly, coals and solid residues from the supercritical toluene extraction of coal liquids from two Nova Scotia coals, at 400°C and 13.8 MPa, are examined. The coals have similar petrographic compositions but are markedly different in rank. They are vitrinite rich (80.4% and 80.6%, respectively) with moderately high inertinite contents (12.4% and 14.4%), relatively poor in liptinite macerals (6.2% and 4.2%) and contain very little mineral matter (1%). The vitrinite reflectance indicates ranks of high volatile bituminous A and C, respectively. The high volatile bituminous A coal has a high reactive maceral content. Together with its superior rank this makes it a potentially better feedstock for coal liquefaction. The residual products from supercritical toluene extraction are predominantly mixed optically isotropic chars

32.2% and 54%), and anisotropic semicokes (64.4% and 45.0%) from vitrinite. The reflectance of the isotropic vitrinite chars from both residues (0.86%, average) is equivalent to a high volatile bituminous A coal. Anisotropic semicokes are more abundant in the residue from the higher ranking, vitrinite rich coal. This residue also contains liptinite macerals which are usually absent from coal liquefaction residues. The abundance of anisotropic semicoke, which is known to retard liquefaction, and the presence of liptinite macerals in the solid products from a coal with a high potential for liquefaction, suggest there was incomplete contact between the coal particles and the supercritical gas, and possibly, a deficiency of hydrogen, in the reactor during that particular experiment.

Feedstocks and residues from coal-bitumen coprocessing experiments, also conducted by Raylo Chemicals Ltd. are examined. A vitrinite rich sub-bituminous coal, the product of heating the coal in anthracene oil, in hydrogen, for one hour at 450°C, and the residues from coal, bitumen and coal/bitumen hydrogenation experiments, also conducted at 450°C, for one hour, are analysed petrographically and by SEM-EDS. Heating the coal in anthracene oil severely alters the petrographic character. The vitrinite reflectance of the altered coal (1.67% R_0) is equivalent to that of a low volatile bituminous coal. Some of the vitrinite softens and forms optically anisotropic semicoke (2.8%). Liptinite and semi-inert macerals react with the anthracene oil, and are absent from the residue. The solid products of bitumen hydrogenation are mostly anisotropic semicokes (93.4%) and the coal hydrogenation solid product is almost entirely composed of anisotropic semicoke (99%). The residue from coprocessing of coal and bitumen comprises isotropic chars derived from the coal (42.0%) and anisotropic semicokes (57.4%); 32.2% is derived from vitrinite and the remaining 25.2% comes from the bitumen. The optical characters of the vitrinite derived components and the bitumen derived components suggest that, under the operating conditions used for this experiment, the addition of bitumen during coal liquefaction, retards semicoke, formation in vitrinite, but semicokes form unhindered from bitumen.

The Nova Scotia Research Foundation Corporation supplied five coals for petrographic analysis. The samples of coal from the Lingan Mine are petrographically similar. They are vitrinite rich coals (79.7% to 82.8%) with appreciable amounts of inertinite macerals (9.0% to 10.2%), some hydrogen rich liptinites (6.2% to 8.2%) and variable mineral matter contents (3.9% to 0.8%). The reflectance of the vitrinite (0.71%, average) indicates that they are of high volatile bituminous B rank. The two samples of coal from the Prince Mine have similar high volatile bituminous B/A ranks and petrographic compositions that closely resemble those from the Lingan Mine. They are also vitrinite rich (79.7%, average) with inertinites ranging from 8.0% to 11.4%, liptinites in the order of 8.0% to 5.8%, and 3.4% mineral matter (average). Similar ranks and petrographic compositions suggest that the five coal will produce similar coal liquid yields on liquefaction.

A single coal feedstock was submitted for petrographic analysis by the Saskatchewan Research Council. Petrographically, it is a huminite rich (75%) lignite (reflectance, R_0 random, 0.32%) with relatively few liptinite (5.4%) and inertinite 7.6%) macerals and contains a small amount of mineral matter (2%). The abundance of structured huminite macerals, which are the most reactive of the huminites, and a high ratio of reactive (87.2%) to inert (7.95%) macerals, render the coal suitable for liquefaction, despite its low rank.

Canmet supplied one sample of catalyst-impregnated coal, three coal-oil feed mixtures (of which only one was analysed), four reactor samples and seventeen distillation residues from their coal-oil coprocessing programme, for petrographic analysis. The feed coal is a vitrinite rich (88.0%) sub-bituminous C/B coal (reflectance, R_0 random, 0.42%) with 6.2% inertinite, 2.0% liptinite macerals and 2.4% mineral matter (clays and pyrite). The coal in the toluene extracted coal-oil feed mixture is significantly different from the dry feed coal. Liptinite macerals (hydrogen rich, reactive precursors of coal-oils) are absent, and the reflectance of the vitrinite is higher at 0.51% indicating a rank of sub-bituminous C bordering on high volatile bituminous. This suggests that the liptinite and vitrinite macerals reacted with the bitumen prior to liquefaction or that toluene removes the more soluble oils altering the chemistry of the macerals.

The samples extracted from the reactor, after the liquefaction experiments were completed, contain coaly particles and bituminous solid products (63% to 97.5%) that are principally derived from bitumen. These are partially soluble in toluene and they are weakly reflecting optically isotropic residues, not anisotropic semicokes, which are a common cause of reactor fouling. The concentration of coal particles in the residues varies with the residence time.

The solid residues from distillation of the liquefaction products also contain coaly particles (vitrinite and inertinite macerals) embedded in an isotropic bituminous matrix similar to that found in the reactor samples. Some of the bituminous matrix is toluene soluble and therefore contains asphaltenes and preasphaltenes and it contains substantial amounts of a light brown oil. While the proportions of these various constituents vary from sample to sample, there does not appear to be any strong relationship between petrographic composition and variations in reaction conditions. However, the reflectance of the vitrinite particles increases as the reaction temperature increases. This is an indication of the degree of chemical alteration of the vitrinite. At low reaction temperatures, (t-50 and t-25) weakly reflecting vitrinites in the distillation residues indicates the prescence of hydrogen rich oils. Residues generated at standard temperatures (t) have a higher vitrinite reflectance which indicates that more coal derived oils were removed from the vitrinite during coal-oil coprocessing.

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DEFINITION OF TERMS

Coal maceral:	Microscopically recognisable constituents of coal derived by diagenesis and metamorphism of vegetal matter.	
Reflectance:	Percentage of light reflected from the polished surface of vitrinite or huminite macerals, relative to a standard of known reflectance. Related to refractive and absorptive indices. Commonly used a rank parameter for high rank coals. Maximum (R_0max) and minimum (R_0min) reflectance values can be recorded on oriented samples. R_0 random (R_0random) is generally recorded on particulate samples.	
Bireflectance:	The difference between R_0max and R_0min; related to refractive and absorptive indices.	
Coke:	Optically anisotropic products of bitumen or vitrinite processed at temperatures greater than 600°C. Similar optical textures to semicoke.	
Semicoke:	Optically anisotropic product of bitumen or vitrinite (or huminite) processed at temperatures less than 600°C. Optical textures range from mosaic to coarse-flow domains.	
Photomicrography:	P.P.L.:	Plane polarised light
	1/2 x N:	Partially crossed polars (used to identify optical textures of semicoke and coke).
	x 250, x 500:	Powers of magnification used in microscopy.

INTRODUCTION

The demand for relatively expensive coal derived synfuels and upgraded heavy oils and bitumens has been reduced as a result of the significant decrease in the price of conventional oil and a worldwide oversupply. However, the technological research into synfuels production using lower rank Canadian coals, prompted by the move towards energy self-sufficiency, is still underway in Canada, and petrographic investigations of coals and the solid products from a variety of coal liquefaction processes, have been continued. This report deals with Phase III (1982-83) of the petrographic studies of coal feedstocks and solid residues generated by Canmet sponsored research groups.

Previous petrographic studies on coals and solid residues from a variety of coal liquefaction processes have demonstrated the importance of the type and rank of coal used and the experimental conditions in controlling the formation of optically anisotropic semicoke in the solid residues. These materials are a common cause of reactor fouling and lower the yield of coal liquids, (Shibaoka and Ueda, 1978). These studies were conducted by the Energy Research Unit in 1980-81 under D.S.S Contract No. OSU80-00088. They were continued, during 1981-82, (D.S.S. Contract No OSU81-00105) with emphasis on the characterisation of solid residues from the coprocessing of coals and coal derived oils or bitumens. Petrographic methods, aided by energy dispersive x-ray spectrometry - scanning electron microscopy, were used to define those portions of the solid residues derived from coal as opposed to oil. The present study involves petrographic studies of lignites, subbituminous and high volatile bituminous coals and the solid residues from a variety of coal liquefaction processes generated by the following Canmet sponsored research groups:

- Raylo Chemicals Ltd., (Raylo)
- Nova Scotia Research Foundation Corporation, (NSRFC).
- Saskatchewan Research Council, (SRC)
- Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, (Canmet).

Raylo Chemicals Ltd. continued their work on supercritical gas extraction of coal using supercritical toluene to extract liquids from high volatile bituminous coals. Two coal feedstocks and two solid residues were analysed. In addition, they conducted coal-oil coprocessing experiments using Athabasca sub-bituminous coal and bitumen. A coal feedstock and four residues were examined. Altogether, nine samples were studied and an estimated 13.3 equivalent analyses were carried out. The results are discussed in Chapter 3.

The Nova Scotia Research Foundation Corporation provided five coal liquefaction feedstocks from Nova Scotia, two from the Prince Mine and three from the Lingan Mine. Five analyses were conducted; these are discussed in Chapter 4.

The Saskatchewan Research Council provided one sample of Saskatchewan lignite on which one complete analysis was performed. The results are given in Chapter 5.

The Energy Research Laboratories at Canmet, continued studies on coal/bitumen coprocessing. One coal, one coal-oil feed mixture, four samples of the toluene insoluble reactor contents and eighteen distillation residues were studied petrographically. Twenty four samples were analysed; a total of 44.5 equivalent analyses were carried out; the results are discussed in Chapter 6.

Scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDS) was conducted on nineteen composite samples of the residues generated by Canmet and on seventeen of the composite samples provided by Raylo. A total of eighty one analyses were conducted and these are discussed in Chapter 7.

General conclusions and recommendations for future work are discussed in Chapter 8. Petrographic terms are defined on page iv.

The objectives of these studies are fourfold. Firstly, to evaluate the liquefaction potential of coal feedstocks by studying the effects of petrographic composition on coal liquid yields. Secondly, to characterise the components of the insoluble carbonaceous residues in the reactor and in the solid products. Thirdly, to identify those components with respect to their precursors. Fourthly, to study the effects of variable operating conditions on the nature of the solid residues and how liquid yields are affected.

The petrography was conducted by J. Potter, W. McDougall, V. Nambudiri and L. Stasiuk. The SEM-EDS work was done by renting time on an instrument from Dowell Canada, Calgary, by B. Kybett. The petrographic equipment was supplied by the Energy Research Unit, University of Regina and the Department of Supply and Services, Canada.

CHAPTER 2

SAMPLE PREPARATION, ANALYTICAL PROCEDURES AND NOMENCLATURE

2.1. Sample Preparation

Coals and residues were prepared by A.S.T.M. methods. Samples with grain sizes coarser than 1 mm were crushed to -20 mesh size (840 μm), separated by riffling to produce approximately five grams of sample. This was mounted in Ciba-Geigy epoxy resin in 25 mm diameter moulds. The epoxy was allowed to set in a vacuum oven, at 50°C. The mounted, particulate samples were ground on carborundum grits (600, 400, 320 and 220 respectively), and polished with 2.0 μm, 0.1 μm and 0.05 μm grades of alumina powder, with water, on a rotating, selvyt-covered lap, according to the method described previously (Energy Research Unit, 1981).

Whenever possible, residue samples and coal-oil feed mixtures were prepared and analysed, as received. When excessive amounts of oil were present the samples were difficult to mount, polish and analyse. Consequently, the original sample was, in this case extracted with toluene for twenty four hours, to remove the oil. This was also necessary for samples analysed by SEM-EDS; new samples were prepared especially for this purpose.

2.2. Analytical

2.21. Petrography

2.21.1. Equipment

Coals and residues were examined petrographically, using Leitz 'Orthoplan' polarising, incident light microscopes with 1/2λ accessory plates for coke microscopy, and a Leitz 'Dialux' brightfield and fluorescent light microscope, modified for plane polarised, incident light microscopy, using oil immersion techniques. Quantitative analyses were conducted using Leitz 'clickstop' stages and Swift automatic point counters. Reflectance measurements were obtained with a Leitz 'Orthoplan' MPV II polarised, incident light system.

2.21.2. Analytical methods.

Petrographic analyses were conducted according to standard I.C.C.P. practices. Quantitative analyses were carried out using the point count method (accuracy ±2%) and reflectance determinations were based on the average of one hundred measurements recorded on vitrinite in the coal feedstocks and vitrinite derivatives in the residues. Because of grain size restrictions, random reflectance (R_0random) was measured, not maximum reflectance as is customary in coal rank determinations. The random reflectance is used to indicate relative differences in the ranks of vitrinite and vitrinite chars.

2.21.3. Nomenclature

Petrographic analysis of coal feedstocks is based on the I.C.C.P. nomenclature for brown coals (1971) and hard coals (1963, 1971). These are given in Tables 2.1 and 2.2. They have been modified to include the term 'maceral type' which describes the principal huminite and vitrinite macerals.

Petrographic analysis of the residues from coal liquefaction or coal-bitumen coprocessing is based on the optical character, morphology

Maceral group	Maceral Type	Maceral	Submaceral+
Huminite	Structured	Textinite Ulminite	Texto-ulminite Eu-ulminite Levigelinite Porigelinite Phlobaphenite Pseudophlobaphenite
	Unstructured	Gelinite Corpohuminite	
	Groundmass	Attrinite Densinite	
Liptinite		Sporinite Resinite Cutinite Suberinite Alginite Liptodetrinite Chlorophyllinite	
Inertinite		Fusinite Semifusinite Macrinite Sclerotinite Inertodetrinite	

+ Incomplete, can be expanded as desired.

Table 2.1. I.C.C.P. Nomenclature applied to brown coals (1971), (modified)

Maceral Group	Maceral	Maceral type	Submaceral+	'Old' nomenclature
Vitrinite	Telinite	Structured	Telinite Telocollinite	Vitrinite A
	Collinite	Unstructured	Gelocollinite Corpocollinite	
		Groundmass	Desmocollinite	Vitrinite B
	Vitrodetrinite			
Liptinite	Sporinite Resinite Cutinite Alginite Liptodetrinite			Exinite
Inertinite	Fusinite Semifusinite Macrinite Micrinite Sclerotinite Inertodetrinite		Pyrofusinite Degradofusinite	

+ Incomplete, can be expanded as desired

Table 2.2. I.C.C.P. nomenclature applied to hard coals, (1963, 1971), (modified)

and reflectance of the components. The components are classified as 'bituminous', 'coal derived' or 'mineral matter'. Each group is then subdivided according to whether the constituents are optically isotropic chars or anisotropic semicokes. Details are given in Table 2.3.

References to coal rank are based on A.S.T.M. rank categories and on the degree of coalification according to component (McCartney and Teichmuller, 1972). These are indicated in Table 2.4. The term reflectance usually refers to the mean maximum recorded reflectance of vitrinite A, which is measured on ancentated block samples or on particulate samples when the particle size allows the operator to rotate the sample during measurement. When this is not possible, random reflectance, R_0 random, is measured. The result is fractionally lower than the maximum reflectance. This is still considered a good relative rank indicator.

2.22. Trace element analysis by S.E.M.-K.E.V.E.X.

Trace element analysis can be used to help identify coal macerals, coke residues and mineral matter. Most chemical analysis techniques are not suitable because they can only be used on bulk samples. Previous work (Energy Research Unit, 1981, 1982) has shown that Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) can be used successfully to supplement light microscopy analysis, since semiquantitative analyses for trace elements can be made on small specific surface areas.

Samples for which it was felt that SEM-EDS would provide useful information were identified during the normal petrographic analysis with light microscopes. The specific subject areas were subsequently

Origin	Species	Optical Character
Bituminous	Matrix	- isotropic* - anisotropic**
Coal	Vitrinite	- isotropic* - anisotropic**
	Inertinite	- isotropic - anisotropic
	Liptinite	
Mineral Matter	Metallic sulphide Clays Quartz	

* char ** semicoke

Table 2.3. Classification of coal liquefaction and coal-bitumen coprocessing residue components

Rank. USA.		Reflectance % R_0max	Carbon d.a.f. vitrinite	Bed moisture	Heating value Kcal/Kg. (Moist,mmf)*	Volatile matter (dry,mmf)*
Peat		0.2				
						68
Lignite						64
		0.3	60	75		
						60
				35	4000 (7200 Btu)	56
Sub-bituminous	C	0.4				52
			71	25	5500 (9900 Btu)	
	B					48
		0.5				
	A					44
		0.6		8-10	7000 (12600 Btu)	
High volatile bituminous	C		77			40
		0.7				
	B					36
		0.8				
	A					32
		1.0				
Medium volatile bituminous						28
		1.2				
			87		8650 (15500 Btu)	24
		1.4				
Low volatile bituminous						20
		1.6				
		1.8				16
Semi anthracite		2.0				12
Anthracite			91		8650 (15500 Btu)	8
		3.0				
		4.0				4
Meta anthracite						

Table 2.4. Classification of coals by rank on the basis of different physical and chemical rank parameters after Stach (1975), (modified)

located, and marked with an eccentric diamond indentor fixed to the objective of a microscope (at 500X). Photomicrographs and graphic surface maps were made to facilitate relocation of these specific subject areas. These methods were discussed in detail in Phase 1 (Energy Research Unit, 1981).

The samples were coated with gold, and examined in a Cambridge Stereoscan 100 SEM with a KEVEX 7000 EDS system (Dowell of Canada, Calgary). The conventional SEM image provided no useful information because the samples were polished, but the marked subject areas could be located, and the specific portion of interest in these subject areas pinpointed using the photomicrographs and graphic surface maps. Sometimes, because of large differences in hardness, which produced irregularities in the differnet coal particles could be identified in the SEM image and correlated with the photomicrographs. These were used to verify that our locating system was accurate.

Spot and area (roster) analyses (10Kev, 50 seconds) were made for all trace elements that could be detected, using the Quantex microanalysis software system on the KEVEX 7000, with MAGIC V quantitative corrections. Elements with atomic numbers greater than 10 (Ne) could be analysed. It was assumed, since ultimate analyses for the specific areas of interest were not available, that carbon, hydrogen and nitrogen and oxygen were "oxygen". Since reference samples for coal are not available the results are only semiquantitative, but can be used for comparisons between (similar) samples.

The repeatability of the analyses was checked by doing duplicate determinations, immediately, on larger and smaller areas of the same maceral particle, and by complete removal and replacement of the sample in the instrument. The repeatability was within the accuracy parameters produced by the Quantex/MAGIC microanalysis system, ± 0.01%.

Element mapping could only be done in the TV mode, and, because of the limitations of the instrument, did not provide useful information.

CHAPTER 3

CHARACTERISATION OF COALS AND RESIDUES FROM COAL LIQUEFACTION EXPERIMENTS CONDUCTED BY RAYLO CHEMICALS LTD.

3.1. Introduction

Raylo Chemicals Ltd. provided coal feedstocks and residues from the supercritical toluene extraction of Nova Scotia coals and from coal-bitumen coprocessing experiments that were conducted during 1982-83 under D.S.S. contracts 26SQ.23440-2-9098 and 26SQ.23440-29069, respectively.

The supercritical toluene extraction of coal is a continuation of their previous studies on the liquefaction of low rank coals by extraction with supercritical gases. Sub-bituminous coals and lignites, and the residues from these experiments were examined petrographically, under D.S.S. contracts 0SU80-00088 and 0ST81-00105. Under the current contracts two high volatile bituminous coals and two chars were examined; 6.3 equivalent petrographic analyses were carried out. Additionally, one coal feedstock and four residues from coal-bitumen coprocessing experiments were analysed. Seven equivalent petrographic analyses were conducted.

3.2. Supercritical toluene extraction of Nova Scotia coals (D.S.S. File No: 26SQ.23440-2-9098).

3.21. Previous studies of coals and residues from supercritical gas extraction of lignites, sub-bituminous coals and high volatile bituminous coals showed that the relative penetrating power of supercritical gases can be detected by microscopical examination of the solid residues. Certain solvents were more effective than others and the rank type of coal used was also important (Energy Research Unit, 1981). Subsequent studies of residues from tetralin/toluene extractions of sub-bituminous coals showed that the effects of varying the relative concentrations of solvents in the mixture, could not be detected petrographically, (Energy Research Unit, 1982). Under the current contract, chars (1 and 2) from supercritical toluene extraction of Nova Scotia coals (1 and 2), at 400°C and at 3.8 mPa (2000 psig), were examined microscopically. The experimental conditions and the sample numbers are identified in Table 3.1.

3.22. Results and Discussion

3.22.1. The Coal feedstocks

The results of the petrographic analyses of the feed coals are summarised in Table 3.2. The petrographic compositions are given by maceral group analyses and random reflectance data are used as relative indicators of coal rank. Detailed analyses are given in Appendix A.

The results show that coals 1 and 2 (STE-205-1-A and STE 205-1-B, respectively) have similar petrographic compositions but are markedly different in rank. They are both vitrinite rich (80.4% and 80.6%, respectively) and mineral matter poor (1% pyrite). They contain appreciable amounts of inertinite macerals (12.4% and 14.2%, respectively). One third to one half of the total inertinite of coal 1 is inert (the remainder being semi-inert), while the inertinite in coal 2 is two thirds inert macerals (fusinite, macrinite). On the whole these coals have low ash contents (3.71% and 4.6%, respectively). Inertinite macerals and mineral matter are the principal constituents of

Sample No. (Raylo)	Coal Feed No.	CHAR No./Experimental Conditions
26SQ.23440-2-9098-		
STE-205-1-A	Nova Scotia 1	-
STE-205-1-B	Nova Scotia 2	-
STE-205-15	Nova Scotia 1	Char 1 produced at 400°C/2000 psig
STE-205-3	Nova Scotia 2	Char 2 produced at 400°C/2000 psig

Table 3.1. Sample numbers and experimental conditions for supercritical toluene extraction of Nova Scotia coals by Raylo Chemicals Ltd.

	Coal 1	Char 1*	Coal 2	Char 2**
Vitrinite - isotropic	80.4	23.4	80.6	45.2
- anistoropic	-	66.4	-	45.0
Inertinite	12.4	7.4	14.2	8.8
Liptinite	6.2	1.4	4.2	-
Mineral Matter	1.0	1.4	1.0	1.0
	100%	100%	100%	100%
Reflectance (% R_0 random)	0.79%	0.85%	0.59%	0.87%

* Char from coal 1 ** Char from coal 2

Table 3.2. Petrographic analyses of feedstocks and chars from supercritical toluene extraction of Nova Scotia coals.

coal ash. The higher ash content of coal 2 can probably be attributed to its slightly higher inertinite count, since coals 1 and 2 contain similar amounts of mineral matter. Liptinite macerals are present in both feedstocks; they comprise 6.2% of coal 1 and 4.2% of coal 2. In each case the dominant maceral is sporinite, a good source of hydrocarbon liquids.

The reflectance of the vitrinite is 0.79% and 0.59% for coals 1 and 2, respectively. While the mean reflectance is derived from random reflectance measurements (R_0 random) and not maximum reflectance (R_0max) which is usually measured on orientated samples and correlates with moisture heating value and carbon content (McCartney and Teichmuller, 1972), it is a good indication of relative coal rank levels. The mean reflectance, R_0 random, indicates high volatile bituminous A and high volatile bituminous C, ranks for coals 1 and 2 respectively (see Chapter 2.21.3).

3.22.2. The supercritical toluene extracted coal chars

The supercritical toluene extracted coal chars are referred to as chars 1 or 2 according to the coals from which they were generated (Table 3.1). The petrographic analyses are summarised in Table 3.2 and detailed analyses and descriptions appear in Appendix A. Despite similarities in the petrographic compositions of the coals, the chars 1 and 2 are somewhat different in terms of the relative proportions of their constituents. This is most likely due to differences in the rank (reflectance, R_0 random) of the vitrinites.

Vitrinite derived semicokes are the dominant constituents. These occur in two forms, an optically isotropic, vesicular vitroplast-like material (23.4% and 45.2% of chars 1 and 2, respectively), and optically anisotropic material comprising ultrafine and fine grained, mosaic-textured, semicoke (66.4% and 45.0%). Semicoke formation depends upon the initial rank of the vitrinite. Higher ranking vitrinites have a tendency to produce optically anisotropic semicokes when heated to 380°C in the presence of hydrogen (Energy Research Unit, 1981). Coal 1 contains higher ranking vitrinite than coal 2 and accordingly, char 1 contains more anisotropic semicoke than char 2. The formation of anisotropic semicoke in the solid residue, during coal liquefaction, retards coal liquid production from vitrinite (Shibaoka and Ueda, 1978).

Inertinite macerals are present in both chars. Char 2, produced from the higher inertinite coal 2, contains slightly more inertinite than char 1. Their mineral matter contents are similar. Coal 2 has a higher ash content than coal 1. This is probably due to the higher intertinite count, as inert macerals are important contributors to coal ash.

A most unusual feature is the presence of liptinite macerals in char 1. Liptinites are chemically, the most reactive of all the coal macerals and are not commonly found in coal chars or semicokes formed at 450°C. Normally they are thermally degraded to liquid products and a carbonaceous residue, micrinite, which is subsequently identified with the inertinite macerals. This might suggest insufficient contact of the supercritical toluene with the coal during that particular experiment. Liptinites were, as expected, absent from char 2.

The isotropic, vitrinite derived portion of both chars has a reflectance, R_0 random, of 0.85%; this indicates that they are of similar rank and reflects similar carbon, moisture and heating values (chapter 2.21.3). The supercritical toluene extraction therefore upgraded the isotropic vitrinites in both coals, to the same, higher, rank level. This would be equivalent to the vitrinite of a higher rank coal (high volatile bituminous A). It is possible that this is connected with the formation of the anisotropic semicoke in the residues.

During coal carbonisation, vitrinite is altered chemically, which results in an increase in coal rank, and physically, resulting in molecular ordering producing a quasi-crystalline structure (Blaydon, Gibson and Riley, 1943). This phenomenon occurs only during the carbonisation of higher ranking vitrinites. The net result is the formation of optically anisotropic semicoke in the solid residue (Patrick, Reynolds and Shaw, 1973). It has been shown that similar materials are produced from vitrinite/huminite during the liquefaction of low rank coals. Indeed anisotropic semicoke occurs in both chars from supercritical toluene extracted coal. It is suggested, however, that the anisotropic semicoke does not form from the isotropic char until a rank level indicated by 0.85% R_0 random is attained. The higher ranking vitrinite of coal (initial reflectance: 0.79% R_0 random) would attain this level more quickly than the low ranking vitrinite (initial reflectance: 0.59% R_0 random) of coal 2. This would result in earlier, and ultimately more, semicoke production from coal 1, if the coals were extracted for the same length of time, and it would also account for similarities in the reflectance of the isotropic chars and the differences in the amount of optically isotropic semicoke produced.

3.3. Athabasca Coal/Bitumen Coprocessing (D.S.S. File No. 26SQ.23440-2-9069).

Samples of Athabasca coal feedstock, coal altered by heating in anthracene oil, at 450°C, coke from hydrogenated coal coke from hydrogenated bitumen and coke from coal/bitumen coprocessing at 450°C, in hydrogen, after one hour, were examined petrographically and by SEM-EDS, (see Chapter 7). The samples are identified by the prefix C-B-Co (Coal-bitumen coprocessing) and by -0, -1, -2, -3 and -4,according to the sample numbers used by Raylo Chemicals. Details are given in Table 3.3. The petrographic analyses are summarised in Table 3.4 and detailed analyses and descriptions of each sample are given in Appendix A.

3.31. Athabasca Coal (C-B-Co-0, 26SQ.23440-2-9069-0).

The feedstock, C-B-Co-0, is a vitrinite rich, sub-bituminous coal (Table 3.3). Vitrinite comprises 94.4% of the coal while the other major petrographic constituents occur in minor amounts. Liptinites, the hydrogen rich source of coal derived liquids, constitute only 2% of the coal. Inertinite macerals constitute 2.9%, and mineral matter, in the form of iron sulphide, 0.7% (Appendix A-6). The reflectance, 0.42% R_0 random, indicates a sub-bituminous C-B rank, according to A.S.T.M. classifications (Table 2.4).

3.32. Altered Coal (C-B-Co-1, 26SQ.23440-2-9069-1).

The altered coal, C-B-Co-1, produced by heating coal, C-B-Co-0, in anthracene oil, at 450°C, in hydrogen, for one hour is an isotropic coal char. Altered vitrinite comprises 99.4% of the solid product (Table 3.3). It is mostly optically isotropic, although minor amounts (2.8%)

Sample No:	Description	Experimental Conditions
26SQ.23440-2-9069		
C-B-Co-0	Athabasca coal	-
C-B-Co-1	Altered coal	coal heated with anthracene oil, 1 hour 450°C, in hydrogen.
C-B-Co-2	Bitumen coke	solid residues produced at 450°C in hydrogen, after one hour.
C-B-Co-3	Coal coke	
C-B-Co-4	Coal/Bitumen coke	

Table 3.3. Sample numbering and experimental conditions for coal/bitumen co-processing by Raylo Chemicals Ltd.

Sample No. C-B-Co	-0 SBC[1]	-1 AC[2]	-2 HB[3]	-3 HC[4]	-4 HC/B[5]
Vitrinite					
- isotropic	94.4	96.6	-	1.0	42.0
- anisotropic	-	2.8	-	99.0	32.2
Inertinite	2.9	0.4	-	-	-
Liptinite	2.0	-	-	-	-
Mineral Matter	0.7	0.2	-	-	-
Bitumen					
- isotropic	-	-	6.6	-	0.6
- anisotropic	-	-	93.4	-	25.2
	100%	100%	100%	100%	100%

(catalyst not included in mineral matter)

1. SBC = Sub bituminous coal
2. AC = Coal heated in anthracene
3. HB = Hydrogenated bitumen
4. HC = Hydrogenated coal
5. HC/B = Hydrogenated coal/bitumen

Table 3.4. Petrographic analyses of feedstocks and residues from coal/bitumen coprocessing experiments

have formed vitroplast (Mitchell et al., 1977) and fine grained, mosaic textured, anisotropic semicoke. The reflectance of the isotropic vitrinite char is 1.67% R_0 random. This is the rank equivalent of a vitrinite in low volatile bituminous coal. Liptinite macerals are absent. Inertinites and mineral matter are minor residual components (0.4% and 0.2%), respectively.

Petrographically, the principal effects of heating the coal C-B-Co-0 in anthracene are (i) to cause reaction of liptinite and semi-inert macerals, and (ii) to alter the reflectance of the vitrinite from that of a sub-bituminous C/B rank to a level exhibited by vitrinites in low-volatile bituminous coal. This implies that the vitrinite was thermally altered.

3.33. Bitumen coke (C-B-Co-2, 26SQ.23440-2-9069-3).

The solid residue produced by hydrogenation of the bitumen (C.B-Co-2), used in the coal-bitumen coprocessing experiments, comprises optically anisotropic semicoke (93.4%) and small amounts of isotropic material (6.6%). The results of the petrographic analyses are given in Table 3.3 and detailed in Appendix A-7. The anisotropic semicoke, which is a common cause of reactor fouling and reduced liquid yields, forms directly from the isotropic bitumen, via growth and coalescence of the mesophase, Plate 1, (Shibaoka and Ueda, 1978), and produces coarse grained, mosaic to flow textured semicoke (Plates 2 and 3). The reflectance, 0.42% R_0 random, of the isotropic bitumen, is the same as the vitrinite of the feed coal (C-B-Co-0). The anisotropic semicoke has a reflectance, R_0 max, of 2.3% and a strongly developed bireflectance (R_{max}-R_{min}) of 0.95%. These properties may be useful for identification of the bitumen derived semicoke in C-B-Co-4, the coal/bitumen coke.

3.34. Coal coke (C-B-Co-3, 26SQ.23440-2-9069-3).

The solid product of the hydrogenated coal, C-B-Co-0, is C-B-Co-3, a semicoke which is dominantly optically anisotropic (99%), and exhibits a variety of optical textures. They range from fine grained to coarse grained mosaics (Plates 4 and 5)) to isotropic vitroplast (Plate 6), described by Mitchell et al. 1977. The fine grained anisotropic mosaic textured semicokes dominate (59.2%) but the coarse mosaics represent a significant portion of the residue (25.2%). Unfortunately, these latter materials resemble the coarse grained semicokes in the hydrogenated bitumen C-B-Co-2. This makes identification of the origin difficult, except that it is significant that they form via the mesophase.

The reflectance of the isotropic vitroplast (0.43%, R_0 random) is similar to that of the isotropic bitumen in C-B-Co-2 (0.42%, R_0 random) but lower than the isotropic vitrinite from which it forms (0.66%). The decrease in reflectance is a common property of vitroplast but the low reflectance makes it difficult to distinguish, optically, between vitrinite derived vitroplast and isotropic bitumen. The reflectance of the semicoke in C-B-Co-3, 2.45% R_0 max, is similar to the bitumen coke in C-B-Co-2 and it also has a similar bireflectance, 0.94%.

3.34.2. The constituents of the coal derived coke (C-B-Co-3) and the bitumen derived coke (C-B-Co-2) can be separately identified by petrographic, methods with the exception of a coarse grained, mosaic-textured semicoke. Trace element analysis by SEM-EDS (Chapter 7.2) show that the coal derived variety and the bitumen derived variety have slightly different trace element contents. The coal derived material can be distinguished from the latter, by the presence of aluminum, and the sulphur content is significantly lower than in the bitumen derived solids.

3.35. Coal/bitumen coke (C-B-Co-4, 26SQ.23440-2-9069-4)

The coal derived solids in the hydrogenated coal/bitumen mixture are slightly different from those occurring in pure hydrogenated coal C-B-Co-3. They are dominantly optically isotropic solids, which make up 41.0% of the total residue (Table 3.4). In addition, vitrinite derived anisotropic semicokes with fine grained and ultra-fine grained, mosaic textures (32%) also occur. The reflectance of the isotropic vitrinite, 1.6% R_0 random, is greater than that in C-B-Co-3.

The bitumen derived solids resemble those found in C-B-Co-2, the hydrogenated bitumen coke. These are medium to coarse grained, mosaics and flow textured semicokes which constitute 25.8% of the total residue C-B-Co-4. The reflectance of the anisotropic semicoke, 2.4% R_0 max, and the bireflectance, 0.95% are also similar to those measured on the hydrogenated semicoke in C-B-Co-2.

3.36. It appears that when coal and bitumen are processed together, the solid products are not a simple mixture of the residues produced by liquefaction of pure coal and pure bitumen. The nature of the solid products from the coal in the coal/bitumen residue, particularly those derived from vitrinite, differ markedly from those formed in coal derived semicoke C-B-Co-3. The optical characters of the coal derived solids and the small grain size of the anisotropic semicokes suggest that bitumen retards the formation of optically anisotropic semicokes from vitrinite. As semicoke formation serves to reduce liquid yields from vitrinite (Shibaoka and Ueda, 1978), it is suggested that bitumen enhances the liquefaction of the coal. On the other hand, the bitumen derived solids are not significantly different from those formed by hydrogenation of bitumen C-B-Co-2, (Plate 7). The coal therefore does not appear to hinder semicoke formation in bitumen or alter the textures of the semicokes formed.

3.4 Conclusions

3.41. Supercritical toluene extraction of high volatile bituminous coals.

The solids products of supercritical toluene extraction of two vitrinite-rich Nova Scotia coals of high volatile bituminous B and C ranks are chars comprising upgraded, isotropic vitrinite char, with a reflectance equivalent to that of a high volatile bituminous A coal, and optically anisotropic semicokes. The latter materials are more abundant in char 1, derived by extraction of coal liquids from the higher ranking coal. It appears that the formation and amount of optically anisotropic semicokes in the solid products of coal liquefaction, depends upon the initial rank of the coal feedstock.

3.42. Coal-bitumen coprocessing.

Petrographic examination of the solid hydrogenation products of pure coal, pure bitumen and the products of coal/bitumen coprocessing show that the residue produced from coal in the coal/bitumen product does not resemble, optically, the product of coal liquefaction, but the bitumen derived solids are optically similar to those produced by hydrogenation of pure bitumen. Coal/bitumen coprocessing therefore retards the formation of optically anisotropic semicoke from vitrinite and thereby enhances the liquefaction potential.

CHAPTER 4

PETROGRAPHIC EVALUATION OF COAL LIQUEFACTION FEEDSTOCKS SUPPLIES BY THE NOVA SCOTIA RESEARCH FOUNDATION CORPORATION

4.1. Introduction

Five samples of coal from Nova Scotia were supplied by the Nova Scotia Research Foundation Corporation (NSRFC), for petrographic analysis. These coals were used as feedstocks for coal liquefaction experiments conducted during 1982-83, under D.S.S. Contract No. OSQ81-00039. Three samples are from the Lingan Mine: "I", "J" and "K", and two are from the Prince Mine: "C" and "D". Compositional analysis by maceral group and individual macerals, and rank determinations based on the reflectance of the vitrinite, R_0 random, were carried out.

4.2. Results and Discussion

4.21. The Lingan Mine Coals

Maceral group analyses and reflectance data are recorded in Table 4.1; maceral analyses are given in Appendix B. The coals from the Lingan mine are vitrinite rich coals of high volatile bituminous rank which show minor variations in petrographic character.

The vitrinite maceral group comprises 79.7%, ("J"), and 82.2%, ("K"), of the coal. Liptinite macerals make up between 6.2%, ("J"), and 8.2%, ("I"); these are principally spores with minor cutinite and resinite. Inertinite macerals range from 9%, ("K"), to 10.2%, ("J"); the dominant type being wholly inert fusinite. Mineral matter occurs as pyrite, clay minerals and silica; it is a minor constituent of all three samples, but makes up almost 4% of "J".

Sample No / Maceral Group	Lingan coal "J"	Lingan coal "K"	Lingan coal "I"	Prince coal "C"	Prince coal "D"
Vitrinite A	79.7	82.8	81.6	79.8	79.6
Liptinite	6.2	7.4	8.2	8.0	5.8
Inertinite	10.2	9.0	9.0	8.6	11.4
Mineral Matter	3.9	0.8	1.2	3.6	3.2
Reflectance:					
Mean $R_o$random (vitrinite A)	0.7	0.71	0.72	0.69	0.67
Std. Deviation	0.1	0.1	0.1	0.10	0.10

Table 4.1. Petrographic analyses of coal feedstocks supplied by NSRFC

There are minor variations in the vitrinite reflectance values: 0.70%, "J", 0.71%, "K", and 0.72%, "I", R_0 random (Table 1); these fall within the standard deviation from the mean. Vitrinite reflectance is a rank parameter for high rank coals (McCartney and Teichmuller, 1972) and although the recorded values are random and not maximum reflectance values, commonly measured on orientated block sample (see Chapter 2.21.3), they indicate a rank of high volatile bituminous B (Table 2.4), according to the ASTM classifications.

Coal oils (liquids) have a higher hydrogen to carbon ratio than coals, and the yield of coal liquids is higher from the hydrogen rich macerals. Liptinites contain the most hydrogen, and give the best yield of coal liquids. Vitrinites are not as rich in hydrogen as liptinites. They are, however, the most abundant macerals, and a large percentage of the coal liquids come from them. Given et el. (1975) demonstrated a relationship between the percentage of vitrinite and liptinite (exinite) macerals in the feedstock and solvation of the coal. Inertinite macerals are inert, except for semifusinite which is considered reactive during coal liquefaction (Diessel et al. 1979).

Compositional and rank differences, determined on a relative basis by reflectance measurements, between the Lingan Mine coals are not significantly marked. Because the rank and petrographic compositions of these coals are so similar, one would expect much variation in liquid yields from these samples. If indeed the batch samples did behave differently on liquefaction, one might suggest, on the basis of petrographic composition, that the Lingan "I" would give slightly better yields because it has the highest liptinite maceral content. The coal "J" might produce slightly lower yields owing to a marginally higher inertinite content and slightly lower liptinite content than the others.

4.22. The Prince Mine Coals

The Prince Mine coals are also vitrinite rich coals of high volatile bituminous rank. The vitrinite contents are almost identical both in terms of total vitrinite (Table 1) and the relative proportions of different vitrinites (see Appendix B-2). Total vitrinite is 79.8%-79.6%. Liptinite macerals comprise 8.0% of "C" and 5.8% of "D"; the principal maceral is sporinite with minor cutinite and resinite. Inertinite macerals comprise 8.6% of "C" and 11.4% of "D". Two thirds of the inertinites in "C", and over half in "D", are semi-inert. Both samples have similar and appreciable mineral matter contents (3.6 and 3.2%, respectively) comprising framboidal pyrite, clays and quartz.

The mean reflectance, R_0 random, for both "C" and "D", is 0.69% indicating a high volatile bituminous C, bordering on high volatile bituminous B, rank, (Table 2.4).

The two samples are fairly similar in petrographic character. The main differences lie in the inertinite and liptinite abundances. The "C" sample contains appreciably more liptinite (8.0%) than "D" (5.8%), and less inertinite (8.6% versus 11.4%). The evidence relating to petrographic character and its effect on liquefaction discussed on the previous page (4.21.), suggests that the potential of "C" to generate hydrocarbons will be greater than the "D".

4.23. Comparison between Lingan Mine and Prince Mine Coals

In general, the coals from the two mines are fairly similar petrographically. Lingan "I" and Prince "C" coals are very similar, and so also are Lingan "J" and Prince "D" samples. Slight differences in reflectance of the vitrinites may reflect slightly different carbon, moisture and heating values. Minor differences in the ash contents could also be expected.

4.3 Conclusions

Coals from the Prince and Lingan Mines, Nova Scotia, are similar, petrographically. Minor differences in reflectance and maceral composition may reflect slight differences in ultimate and proximate analyses. These differences are unlikely to produce significant variations in the nature of the liquefaction products or in the coal derived liquid yields.

CHAPTER 5

PETROGRAPHIC EVALUATION OF A COAL LIQUEFACTION FEEDSTOCK SUPPLIED BY THE SASKATCHEWAN RESEARCH COUNCIL

5.1. Introduction

The Saskatchewan Research Council (SRC) supplied one sample of coal that was used as a feedstock for liquefaction experiments conducted during 1982-83, under D.S.S. Contract No. 14SQ 23440-0-9089. A petrographic analysis, comprising maceral analysis and rank determination was conducted.

5.2 Results and Discussion

The petrographic composition of the coal, given by maceral group analysis, and a rank determination based on reflectance of the huminite component, are given in Table 5.1. A detailed maceral analysis is given in Appendix C.

The sample of coal is a huminite rich (85%) lignite with a petrographic composition typical of those from the Estevan area of southern Saskatchewan. There is a small amount of liptinite macerals (5.4%), the inertinite maceral content is quite low (7.6%), and there is a small amount of mineral matter (2.0%), mainly in the form of pyrite, with minor clay minerals. The reflectance of the huminite, is 0.32% R_0 random; this is also typical of the lignites from the Estevan area.

During coal liquefaction, greater yields of coal-derived oils are produced from hydrogen rich macerals. The most hydrogen rich macerals belong to the liptinite group. Unfortunately liptinites occur in relatively small amounts (5.4%) in the SRC feed coal. A large percentage of

% Maceral Group		% Maceral Subgroup	
		Structured:	58.6%
Huminites:	85.0%	Unstructured:	4.0%
		Groundmass:	22.4%
			85.0%
Liptinites:	5.4%		
Inertinites:	7.6%		
Mineral Matter:	2.0%		
	100%		
Reflectance			
Mean % R_0 random		0.32%	
Standard deviation		0.05	

Table 5.1. Petrographic analysis of coal liquefaction feedstock, provided by SRC.

coal derived liquids come from huminite macerals. These are abundant in this coal (85%). Previous studies on the relationships between petrographic composition of the feed coal and liquid yields, (Energy Research Unit, 1981, 1982) have shown the structured huminite macerals are the most reactive of this variable group of macerals. In this case 58% of the huminite macerals are structured varieties, which makes the coal a potentially good feedstock for liquefaction. Inertinite macerals do not generate coal liquids as they are inert or, in the case of semi-fusinite, relatively inert. Semi-fusinite is considered to be reactive during coal liquefaction, (Diessel _et al_, 1978). Inert macerals occur in relatively small amounts. Mineral matter also occurs in relatively small amounts. The catalysing effects of mineral matter have been discussed by Given _et al_., 1975, and Yokono _et al_., 1982.

5.3. Conclusions

The abundance of huminite macerals in the SRC feed coal and in particular the abundance of structured huminites of lignite rank, render the coal suitable for liquefaction. The ratio of reactive components (87.2%) to inert components (7.95%) is high and therefore the potential to yield coal oils should be fairly good.

CHAPTER 6

PETROGRAPHIC EVALUATION OF COALS, COAL-OIL FEED MIXTURES, REACTOR SAMPLES AND DISTILLATION RESIDUES FROM COAL-BITUMEN COPROCESSING EXPERIMENTS SUPPLIED BY CANMET.

6.1. Introduction

Feedstocks, reactor samples and distillation residues from coal-oil coprocessing experiments carried out at variable operating conditions, in a pilot plant reactor, were generated by CANMET. Twenty-five such samples were submitted for petrographic analysis. These comprised one catalyst impregnated feed coal, one bitumen feedstock, two coal-bitumen feed mixtures, seventeen distillation residues and four reactor samples. The feed mixtures were extracted with toluene but only one (290782) produced enough insoluble material for petrographic analysis. One distillation residue (120582) and the four reactor samples were toluene extracted and the insoluble products were examined microscopically. All of the solid distillation products were mounted in epoxy resin, polished and examined 'as received' despite the fact that some of them contained oils. The oil tended to exude from the polished surfaces of the mounted samples and into the immersion oil during microscopical examination. It was therefore necessary to study each sample, clean and repolish each one prior to a petrographic analysis. Each petrographic analysis comprised identification of the components, quantitative compositional analysis and reflectance measurements on at least two of the major components. Twenty four samples were analysed; an estimated 44.5 equivalent analyses were performed. Quantitative trace element analyses were conducted on nineteen samples, using SEM-EDS. Twenty nine analyses were carried out and the results are discussed in Chapter 7.

The reactor samples and distillation residues were generated at specific temperature (t), pressure (p), coal-bitumen concentrations (c) and residence times (r). These are referred to as 'standard' conditions. The actual experimental conditions were unknown, but experimental variations indicated by reference to the standard conditions, eg. 2r = two times the standard residence time. The sample numbers and experimental conditions, thus indicated, are given in Table 6.1.

6.2. Results and Discussion

6.21. Feed coal and feed mixtures

Of the three samples provided, one dry feed coal, impregnated with catalyst, and one toluene insoluble feed mixture, 290782, were analysed. (Sample 190282 did not contain any toluene insoluble material). The results are given in Appendix D (D-1 and D-2).

The feed coal is a vitrinite rich sub-bituminous coal comprising 88.6% vitrinite, 6.2% inertinite macerals and 2.6% liptinites. The remaining 2.4% comprises mineral matter, mostly clay minerals and metal sulphide. The vitrinite reflectance, R_0 random, is 0.42% which indicates a coal rank of sub-bituminous C-B, according to the A.S.T.M. classifications (Table 2.4).

The toluene insoluble portion of the feed mixture 290782 is vitrinite rich (91.6%) with slightly more inertinite (7.8%) than the dry feed, minor amounts of liptinite (0.2%) and mineral matter (0.4%). The vitrinite reflectance, R_0 random, is 0.51%; this indicates a coal of sub-bituminous A rank, according to A.S.T.M. classification, which is higher than the dry feed coal.

Conditions:	Temperature	Pressure	Residence Time	Concentration
Residue samples				
030282	t	p	r	c
140582	t	p	r	c
011281-3	t	p	r	c
221081	t-25	p	r	c
290782	t-25	p	r	c
260882	t-25	p	2r	c
271081	t-50	p	r	c
010682	t+15	p	r	c
151281	t	p	0.67r	c
190282	t	p	r	no coal
120582	t	p	r	0.5c
170582	t	p	r	1.25c
190582	t	p	2r	1.25c
241181	t	p	r	1.25c
250682	t	0.5p	r	c
140782	t	1.25p	r	c
051181	t	1.25p	r	c
Reactor Samples				
190282	t	p	r	no coal
030282	t	p	r	c
120582	t	p	r	0.5c
081281	t	p	2r	c

t = standard temperature, p = standard pressure

c = coal concentration (wt. %, d.a.f.) r = standard residence time

Table 6.1. Experimental conditions under which distillation residues and reactor samples were generated by Canmet

The dry, catalyst impregnated feed coal and the toluene insoluble coal from the feed mixture are different in petrographic composition and rank. The total vitrinite in the feedmixture is higher by 3%. This may be due to sampling variations or it could be a relative difference attributable to the additional mineral matter in the feed coal which contains an inorganic mineral catalyst. The liptinite content of the feed coal is greater by a significant 2%. Liptinite macerals are hydrogen rich and chemically, they are the most reactive of the coal macerals. The face that the toluene extracted feed mixture contains only 0.2% suggests that the liptinites are either soluble in the bitumen, or soluble in the toluene, used to extract the coal-bitumen mixture.

The reflectance of the vitrinite in the toluene insoluble feed mixture (0.51%) is significantly higher than that of the 'dry' coal feed (0.42%). A 0.1% difference in reflectance, R_0 random, is a strong indication that the vitrinite in the feed mixture has been altered chemically. An increase in reflectance from 0.42% to 0.51%, R_0 random, results from a decrease in the volatile matter content and an increase in the carbon content, comparable to a change in the rank of the vitrinite from sub-bituminous C-B to sub-bituminous A rank equivalent. It appears that the vitrinite, as well as the liptinites, may also have reacted with the bitumen in the feed mixture or that the more soluble components were extracted by toluene, thereby altering the reflectance and the rank of the coal.

6.22. Reactor Samples. 030282, 120582, 081281 and 190282

Four reactor samples were extracted with toluene and the insoluble residues were analysed petrographically. The results are given in Table 6.2. Variations in experimental conditions from standard temperature, pressure, residence time and relative concentrations of coal and bitumen, are indicated at the top of the table.

The toluene insoluble portions of the reactor samples contain four major components. The dominant constituent is bituminous material that is optically, isotropic, weakly reflecting, has ultrafine mineral matter dispersed through it and hosts coaly particles (Plate 8). The other constituents, in decreasing order are a vitrinite char that is dominantly isotropic with a reflectance 0.05% to 0.13% higher than the feed coal (Plate 8); inertinite macerals from the coal, and mineral matter that is dominantly metallic sulphide.

The isotropic bituminous matrix is the dominant component in all four reactor samples, including 190282, which did not contain coal in the initial charge. It is therefore considered to be the toluene insoluble liquefaction product of the bitumen. Similar material was detected in reactor samples and residues from the liquefaction of coal-oil mixtures generated by Canmet in 1981-82. A large proportion of this isotropic matrix was benzene soluble and was therefore presumed to contain asphaltenes and preasphaltenes, (Energy Research Unit, 1982).

The reactor contents of 030282, after liquefaction at standard conditions, are 63.3% bituminous products, 35.3% coal derived and 1.3% mineral. A similar sample, 120582, extracted from the reactor after liquefaction under similar conditions, but when only half the initial coal concentration was employed, is 72.6% bituminous and is 23% coal (it is interesting to note that the concentration of vitrinite, 17.2%, is almost half that of the previous sample, 32.3%). The reactor sample,

Sample no.	030282	120582	081281	190282
Conditions	Standard	0.5c	2r	no coal
Bituminous:	*Tol. insol.	*Tol. insol.	*Tol. insol.	
Isotropic Residual Matrix	63.33	72.6	96.0	96.0
Anisotropic Residual Matrix	-	-		1.5
Vitrinite:				
Isotropic	32.33	17.0	3.0	-
Anisotropic	-	0.2	0.3	-
Inertinite:				
Isotropic	3.0	5.8	0.3	-
Anisotropic	-	0.2	-	-
Mineral:				
Metallic	1.33	4.2	0.3	1.5
Other	-	-	-	1.0
R_0(random) Matrix				
R_0(AV)%	0.22	0.33	-	0.29
Std. Dev.	0.01	0.02	-	0.01
Vitrinite:				
R_0(AV)%	0.55	0.50	0.47	-
Std. Dev.	0.05	0.05	0.04	-

* Toluene insoluble residue

Table 6.2. Petrographic analyses of reactor samples, generated by Canmet

081281, generated when the residence time was doubled, contains very little coal (3.6%) and is almost totally bituminous (96.0%). It contains the same amount of isotropic bituminous material as sample 190282 where no coal was originally present. These values are shown graphically in Figure 6.1.

Sample 190282 has fractionally more anisotropic material than the other reactor samples, 1.5%. The samples are, for the most part, optically isotropic in nature. This suggests that the experimental conditions favour the formation of optically isotropic residues and not anisotropic semicokes, which form at the expense of liquid products.

6.23. Distillation Residues

Solid residues from the distillation of the products of seventeen coal-oil coprocessing experiments were analysed petrographically. In addition, one residue, 120582, was extracted with toluene and the insoluble portion was examined. The results of the analyses are summarised in Table 6.3, together with the variations in standard experimental conditions appropriate to each sample. Details of the analyses and individual sample descriptions appear in Appendix D.

The dominant material in the unextracted distillation residues is a weakly reflecting (mean R_0 random, 0.3%), isotropic, vesicular, bituminous matrix containing coaly particles and sub-micron sized mineral matter (Al, Si, S, Fe, K, Ca) Plate 9. This is similar to the material that dominates the toluene insoluble reactor contents. Previous studies have shown that it occurs in diluted concentrations when extracted with benzene and therefore it contains asphaltenes and preasphaltenes, (Energy Research Unit, 1982). It comprises between

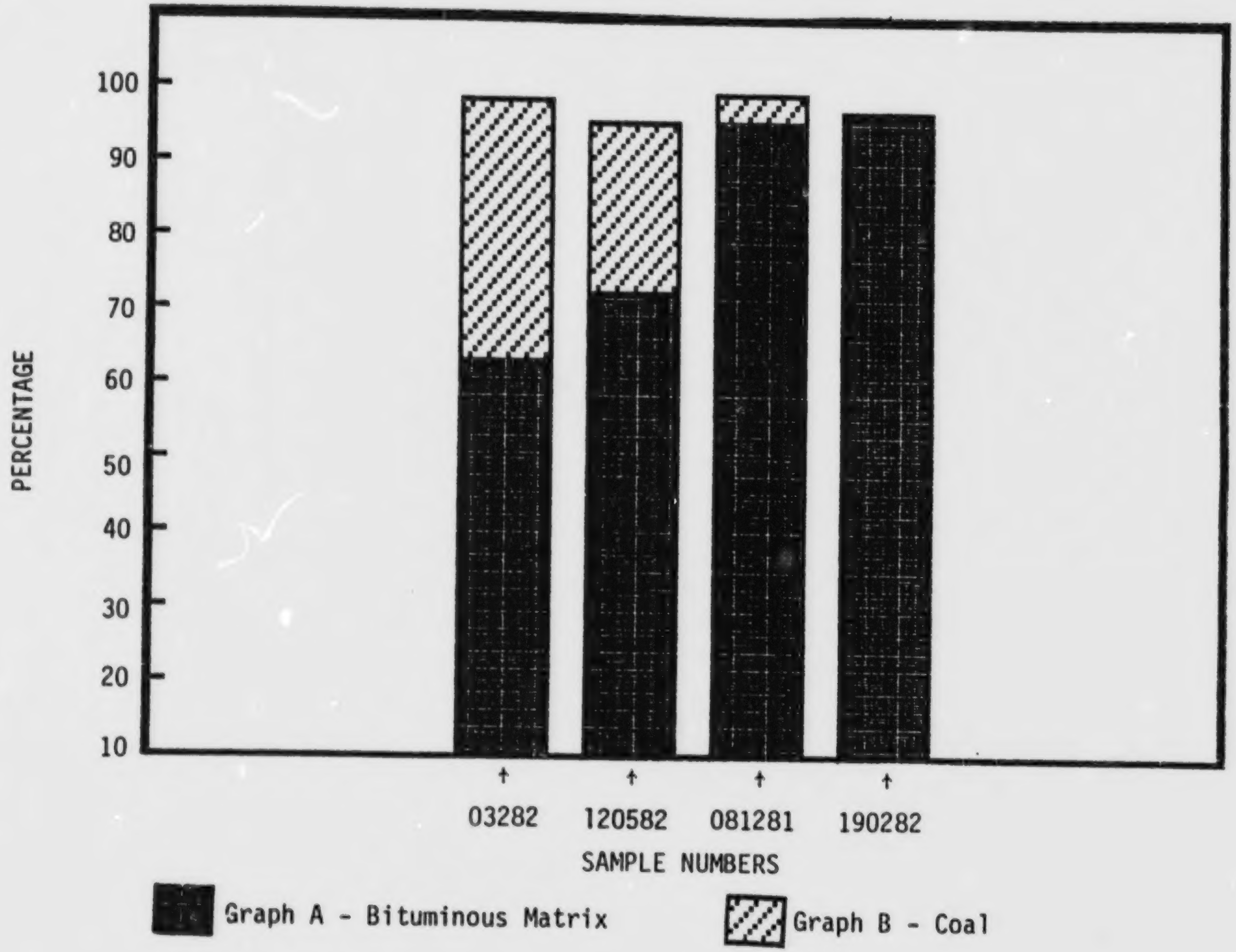

FIGURE 6.1 - Relative abundance of organic constituents in reactor samples

Sample no.	030282	140582	011281-3	221081	290782	260882	271081	010682	151281	120582	120582	250682	170582	241181	190582	140782	051181	190282
Conditions	STANDARD			t-25		t-25, 2r	t-50	t+15	0.67r	0.5c	0.5c	0.5p	1.25c		1.25c,2r	1.25p		No coal present
											Tol.Insol							
Bituminous:																		
Isotropic Matrix	88.8	77.6	91.2	94.6	90.6	95.2	92.0	88.0	94.7	97.3	93.9	94.8	86.4	85.3	86.4	89.4	76.6	94.4
Anisotropic Matrix																		
Mesophase	-	-	-	-	-	-	-	-	-	-	-	0.8	-	-	-	-	1.6	-
Granular Mosaic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.6	-
Vitrinite:																		
Isotropic	3.0	12.4	3.0	4.2	8.0	3.4	7.0	4.2	2.8	1.7	1.9	2.6	6.0	10.0	6.6	5.2	8.6	3.6
Anisotropic	0.2	0.2	-	-	-	-	-	1.6	0.25	-		1.0	-	-	0.2	-	3.2	-
Inertinite	2.0	1.0	0.6	0.6	0.6	0.2	-	0.4	0.25	0.3	1.0	0.4	3.3	2.3	1.8	0.2	3.4	0.8
Mineral																		
Metallic	4.6	8.8	2.2	0.6	0.8	1.2	1.0	5.8	2.0	0.7	3.2	0.4	4.3	2.3	5.0	5.2	3.0	1.2
Other	1.4	-	3.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
% R_0 Random																		
Matrix (Isotropic)																		
% R_0(AV)	0.31	0.35	0.32	0.26	0.25	0.23	0.24	0.44	0.28	0.28	0.32	0.32	0.29	0.36	0.30	0.30	0.24	0.30
St. Dev.	0.03	0.03	0.02	0.03	0.02	0.02	0.01	0.06	0.02	0.02	0.04	0.02	0.03	0.03	0.29	0.02	0.03	0.03
Vitrinite																		
% R_0(AV)	0.49	0.57	0.63	0.52	0.57	0.45	0.51	0.60	0.47	-	0.6	0.57	0.52	0.56	0.61	0.57	0.48	0.61
St. Dev.	0.03	0.08	0.09	0.08	0.07	0.11	0.05	0.07	0.05	-	0.4	0.06	0.09	0.09	0.07	0.09	0.09	0.07

Table 6.3. Petrographic analysis of distillation residues from coal-bitumen coprocessing experiments conducted by Canmet

76.6% and 97.3% of the distillation residues (Figures 6.2a and b), it fluorescences when illuminated with blue-violet light and it has a strong tendency to exude a light brown oil used in coal microscopy. It is slightly soluble in toluene, as indicated by the remnant nature of the toluene extracted residue, 120582. (The 'remnant matrix' resembled the diluted 'D_4' type described in a previous report. (Energy Research Unit, 1982). Coaly particles are hosted by the bituminous matrix. Generally they are less than 50 μm. They comprise vitrinite which has been upgraded in rank, as indicated by the reflectance, (R_0 random, 0.55%) and inertinite particles. Liptinite macerals are absent. The total coal derived materials comprise between 2% and 13.6% of the residues. There are small amounts of coal in residue 190282; no coal was originally present in the charge and so the sample must have been contaminated. (Duplicated samples were prepared which also contained coal).

Given the statistical accuracy of the point count method of compositional analysis, ±2%, there does not appear to be any significant relationship between the amount of coal or bitumen derived components in the distillation residues, and the experimental conditions. Indeed, the three residues run at standard conditions have variable petrographic compositions. Residue 140582, in particular, contains relatively large amounts of coal and mineral matter. But, if the amount of coal derived solids in each of the distillation residues is compared with the average value of 7.3% for the residues generated at standard conditions, some general observations can be made regarding the effects of variations in experimental conditions. Less than half the average coal concentration is present in the distillation residue (120582) from experiments where

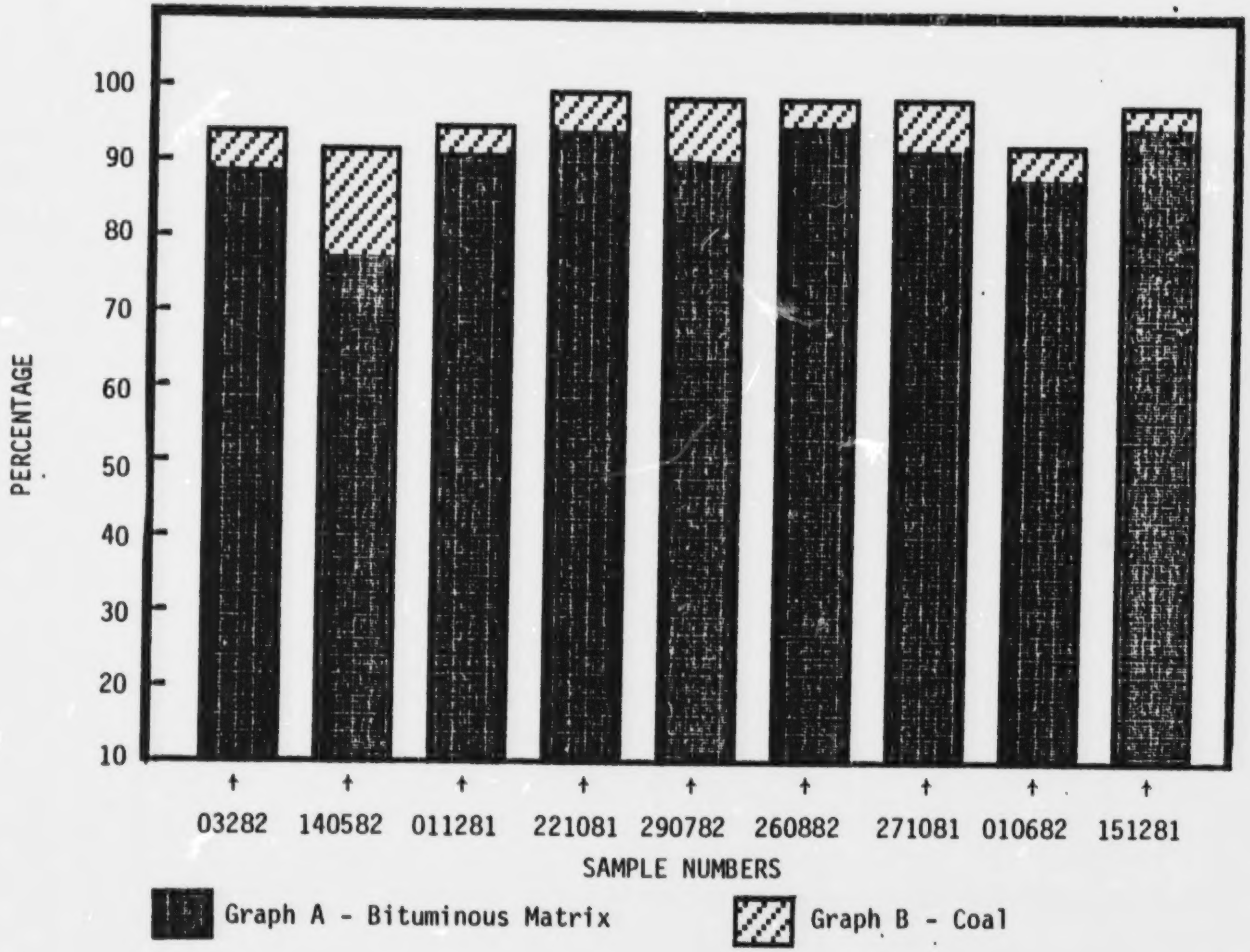

FIGURE 6.2a - Relative abundance of bituminous material and coal in distillation residues.

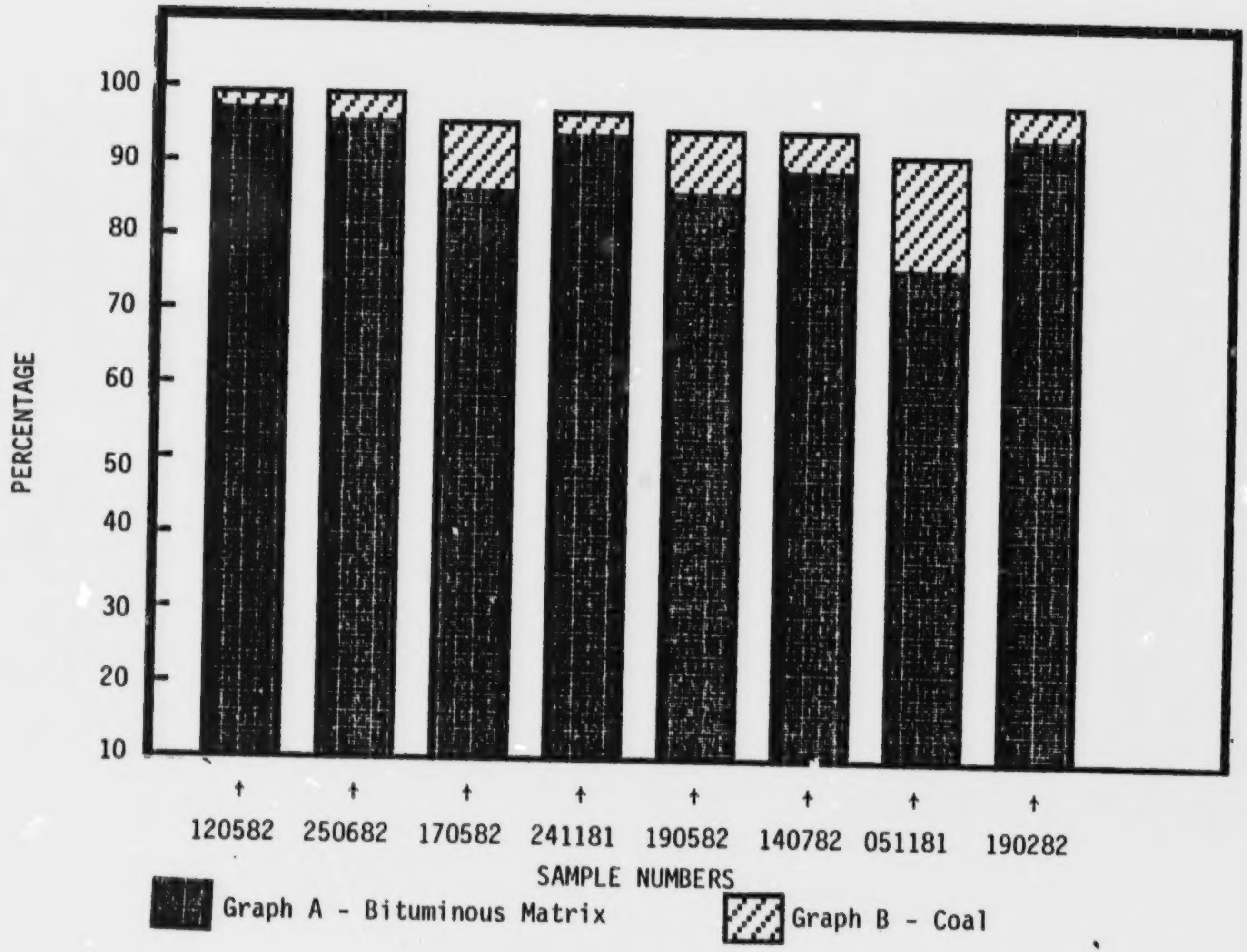

FIGURE 6.2b- Relative abundance of bituminous material and coal in distillation residues.

the coal concentration in the coal-oil charge was halved. A higher than average coal concentration occurs in residues (170582, 241181, 190582) where 1.25 times the coal concentration (1.25c) was used. There is little or no anisotropic semicoke present in any of the residues except for those produced at elevated pressures, (051181), See Figures 6.3a and b and 6.4a and b.

Significant variations in the reflectance, R_0 random, of the bituminous matrix and of the vitrinite were observed. These reflect variations in the chemistry of the organic components with respect to carbon content; the higher the reflectance the higher the carbon concentration in that material. The vitrinite reflectance of the feed coal is 0.42%; the reflectance of the vitrinite char in the residues ranges from 0.41% to 0.61%. These variations in reflectance do not appear to relate to any specific variation in the experimental conditions except for reaction temperature which does appear to affect the bituminous matrix. There is a significant increase in the reflectance of the bituminous matrix with increasing reaction temperature (Figure 6.5). At t-50 and t-25, the matrix is weakly reflecting which implies that hydrogen rich components are still present. This suggests that standard temperatures (t) are required to bring about significant chemical alteration of the matrix, by removing of hydrogen rich oils. A coal concentration of 0.5c and residence time variation of 0.67r also produce very weakly reflecting bituminous residues (120582, 151281) which suggest that higher coal concentrations and longer residence times, such as standard c and r, are required to bring out significant alteration of vitrinite.

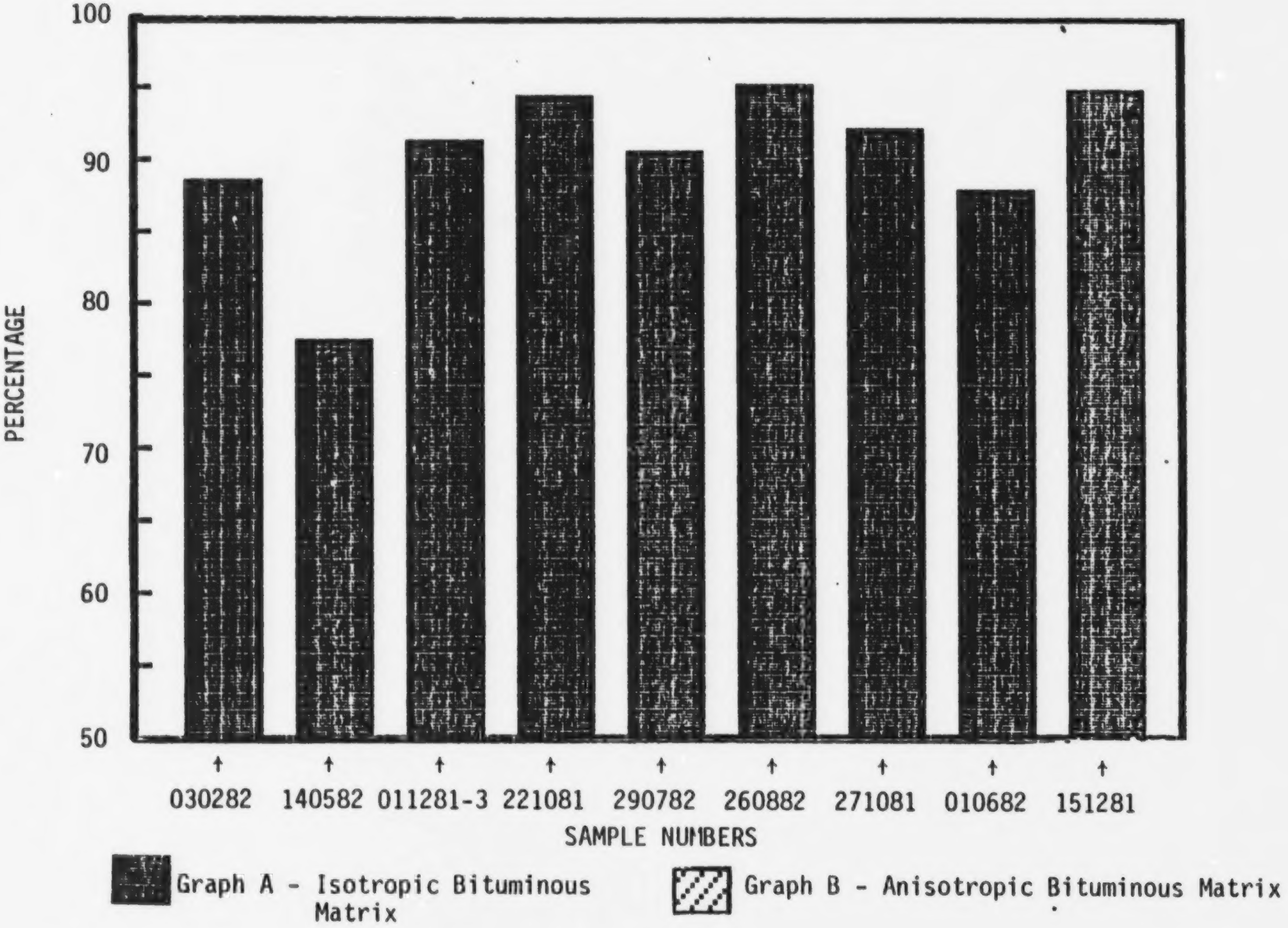

FIGURE 6.3a - Relative abundance of optically isotropic and anisotropic bituminous material in distillation residues.

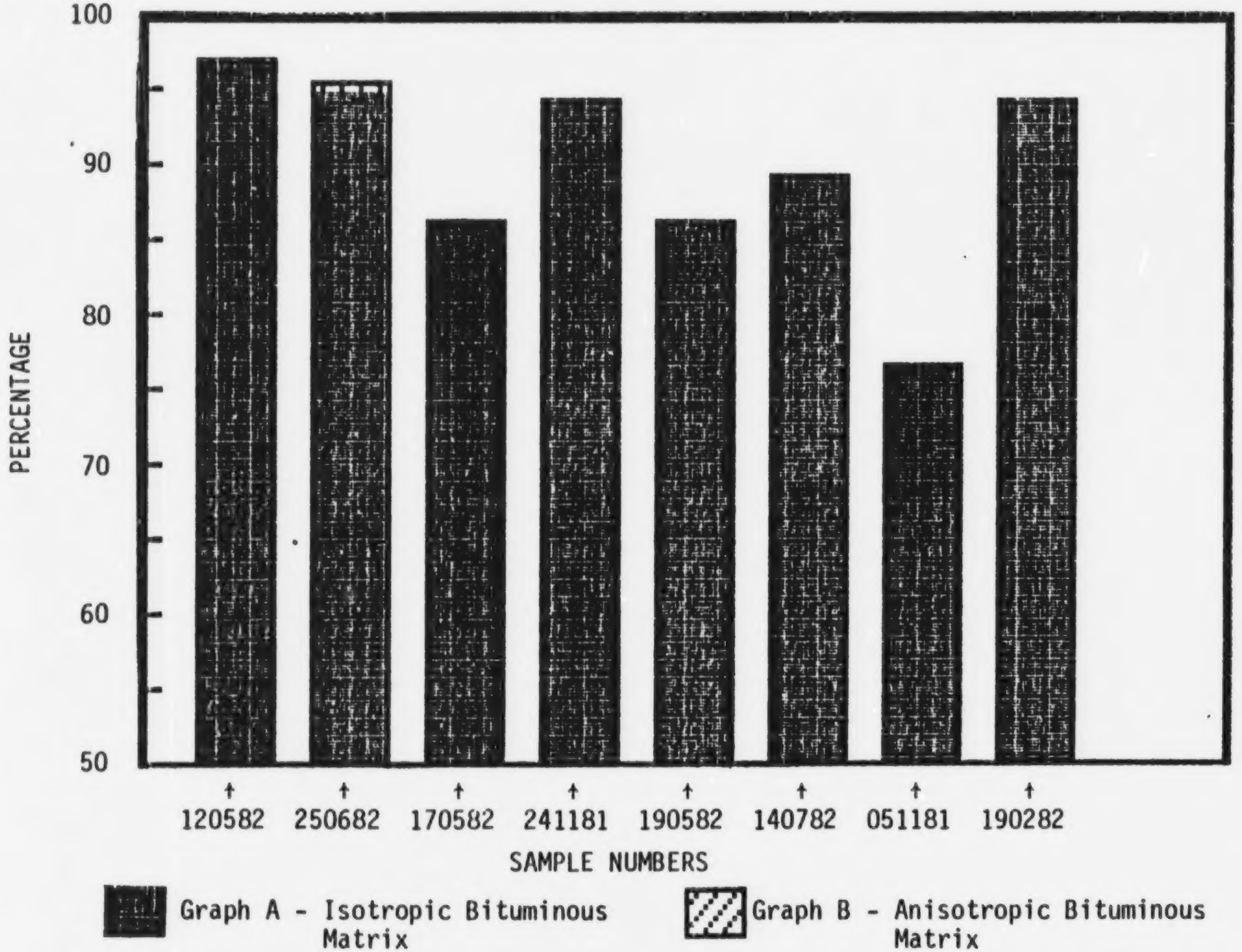

FIGURE 6.3b - Relative abundance of optically isotropic and anisotropic bituminous material in distillation residues.

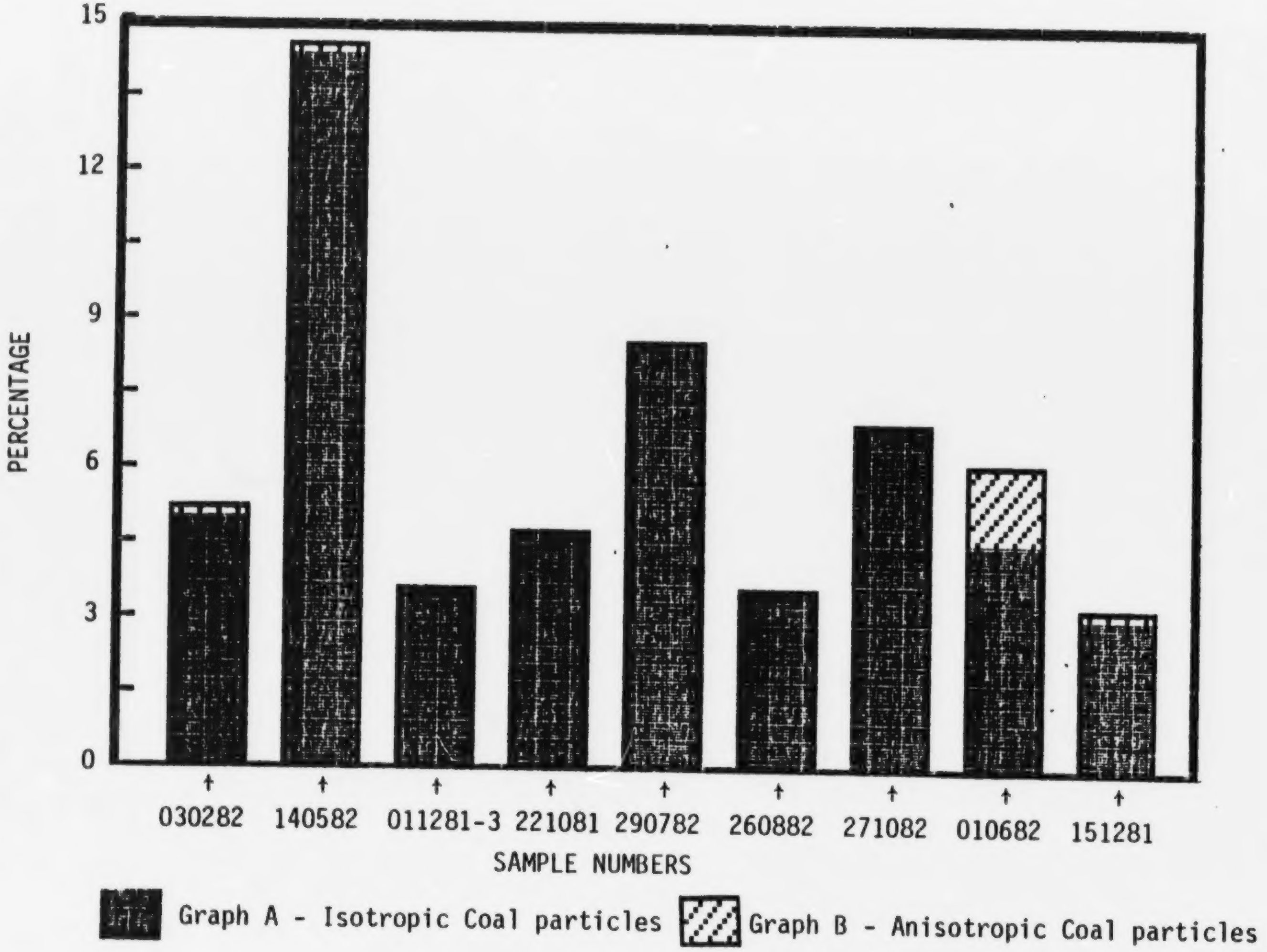

FIGURE 6.4a- Abundance of optically isotropic and anisotropic coal constituents in distillation residues.

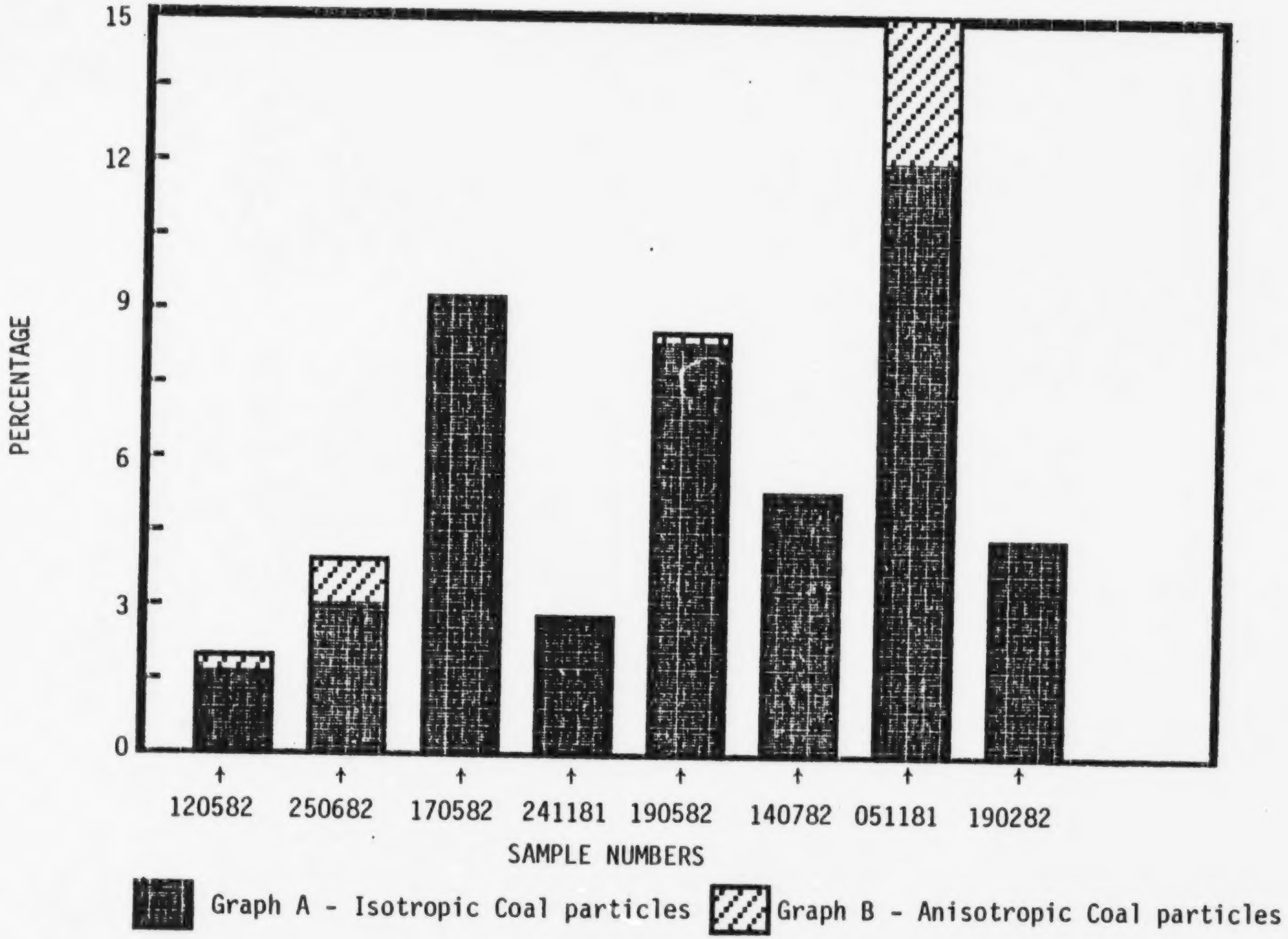

FIGURE 6.4b- Abundance of optically isotropic and anisotropic coal constituents in distillation residues.

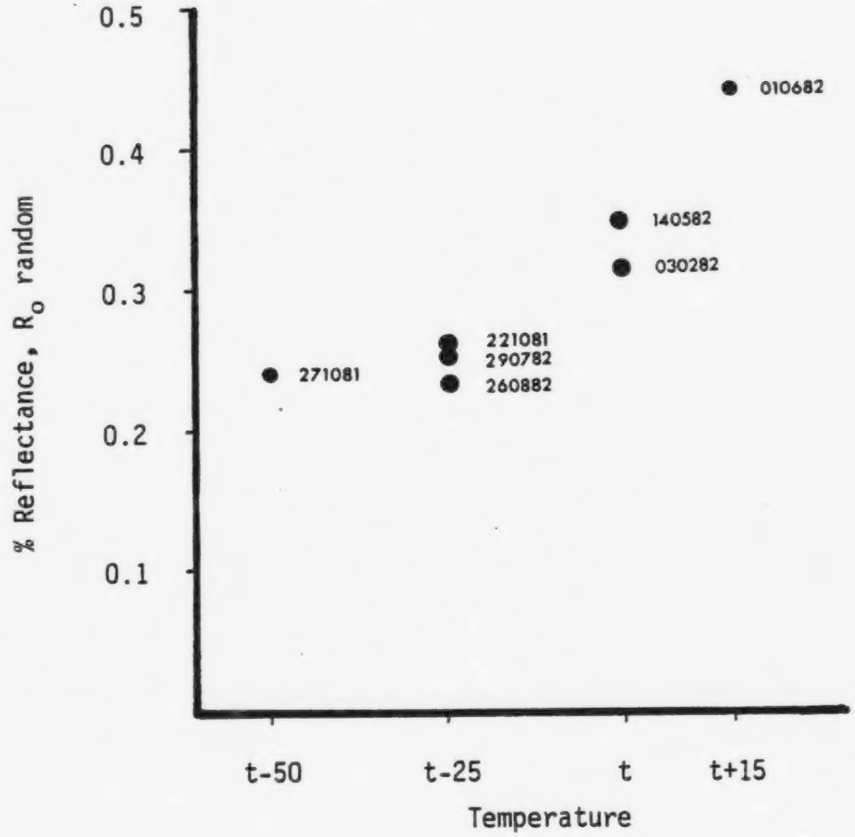

Figure 6.5 - Reflectance, R_0 random, of isotropic bituminous matrix in distillation residues versus reaction temperature

6.4. Conclusions

Petrographic analyses of the dry, catalyst impregnated feed coal and the toluene extracted coal-oil feed mixture (coal) reveal small, but nevertheless important, variations in petrographic composition and significant differences in the ranks of the contained vitrinites. In particular, the absence of liptinite macerals from the feed mixture, and vitrinites with a reflectance level equivalent to sub-bituminous A, or high volatile bituminous C rank coals suggests that, liptinite and vitrinite macerals react either with the bitumen in the feed mixture or with the extracting solvent.

The reactor samples from coal-oil coprocessing contain coaly particles and bituminous solid products that are mostly toluene soluble. The sample from an experiment conducted at standard conditions (t,p,r,c) contains significantly larger amounts of coal (32.3%) than those produced under variable conditions. The amount of coal in this sample, 030282, is approximately two times greater than in 170582, where half as much coal (0.5c) was employed, and it is almost ten times greater than in sample 081281, when the standard residence time was doubled (2r). On the whole the reactor samples are mostly optically isotropic residues (chars) and not anisotropic semicokes which tend to form at the expense of liquid products.

The distillation residues also contain coaly particles, which are upgraded in rank and embedded in an isotropic bituminous matrix that ranges from 76.6% to 97.3% of the residues. A large part of this bituminous residue is toluene soluble, and therefore contains asphaltenes and preasphaltenes, and it contains a light brown oil which exudes into the immersion oil. While the proportions of the major constituents vary from sample to sample, there does not appear to be any significant relationship with variations in the experimental conditions. However, varying the reaction temperature appears to alter the reflectance, and therefore the chemistry, of the bituminous matrix. Weakly reflecting bituminous residues are produced at t-50 and t-25. This implies that considerable amounts of hydrogen rich components are still present and a minimum standard temperature (t) is required to report the hydrogen rich oils.

CHAPTER 7

RESULTS OF TRACE ELEMENT ANALYSES OF COALS AND LIQUEFACTION RESIDUES BY SEM-EDS STUDIES

7.1. Introduction

In previous studies trace element analyses of petrographically selected components of coals and liquefaction residues were used to identify residual components and to trace the precursors. (Energy Research Unit, 1982). The results correlated reasonably well with the petrographic data and they were particularly useful for identifying the amorphous carbonaceous matter in residues from coal-oil or coal-bitumen coprocessing experiments.

Similar studies using SEM-EDS to analyse quantitatively for trace elements were conducted on petrographically selected components of feedstocks and residues supplied by Raylo Chemicals Ltd. and Canmet. Twenty three trace element spectra were obtained for seventeen components in four coals and cokes from Raylo's coal bitumen coprocessing experiments. Twenty nine analyses were carried out on nineteen components of one reactor sample and four distillation residues from Canmet's coal-oil coprocessing programme.

7.2. Results and Discussion

A total of fifty two trace element analyses were obtained on thirty six samples. The results are given in Tables 7.1 to 7.8. The first column in each table identifies the sample number used for petrographic analysis. In the second column, petrographically selected components are identified, and relative weight percentages of major trace elements

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #0	Vitrinite	-	-	7.7	7.2	25.4	4.7	-	-	1.4	53.5	
C-B-Co #3	Isotropic vitrinite	-	-	8.6	9.9	20.0	12.8	-	-	-	48.8	
C-B-Co #0	Structured vitrinite	-	-	8.4	7.1	24.9	5.4	-	-	1.1	53.1	
C-B-Co #1	Structured vitrinite	-	-	6.2	8.0	25.7	5.7	-	-	1.0	53.4	
	Groundmass vitrinite	-	-	7.0	8.4	24.9	5.4	-	-	1.0	53.3	
C-B-Co #0	Inertinite	-	-	7.9	6.8	25.4	6.0	-	-	0.9	53.1	
C-B-Co #1	Inertinite	-	-	8.4	7.3	24.9	6.5	-	-	-	53.0	
	Inertinite	-	-	7.9	6.8	25.9	5.6	-	-	0.3	53.6	

*Cl from mounting resin

Table 7.1. Quantitative analyses of coal/bitumen coal processing residues, generated by Raylo Chemicals

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #3	Fine-grained o.a. semicoke	-	-	9.8	8.4	21.2	10.6	-	-	-	50.0	These are vitrinite derived semicokes
	Fine-grained o.a. semicoke	-	-	8.9	9.8	19.8	12.3	-	-	-	49.0	
	Medium-grained o.a. semicoke	-	-	9.5	8.9	20.3	12.0	-	-	0.3	49.0	" "
	Medium-grained o.a. semicoke	-	-	8.9	9.1	20.6	12.2	-	-	-	49.2	" "
	Coarse-grained o.a. semicoke	-	-	8.8	8.6	21.2	12.0	-	-	-	49.4	" "
C-B-Co #2	Coarse-grained o.a. semicoke	-	-	-	5.5	32.1	7.9	-	-	-	54.4	These are bitumen derived semicokes
	Coarse-flow coke o.a. semicoke	-	-	-	5.2	32.0	8.8	-	-	-	53.9	

o.a. semicoke = optically anisotropic semicoke

*Cl from mounting resin

Table 7.2. Quantitative analyses of coal/bitumen coprocessing residues, generated by Raylo Chemicals

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #3	Mesophase	-	-	9.5	8.9	20.1	12.8	-	-	-	48.7	
C-B-Co #2	Mesophase + isotropic bitumen	-	-	4.4	5.3	29.5	6.8	-	-	-	54.1	
C-B-Co #0	Mineral matter	-	-	9.1	11.9	19.6	5.5	-	-	2.3	51.6	
	Mineral matter	-	-	6.0	11.3	23.3	5.0	-	-	0.9	53.4	
	Mineral matter	-	-	5.3	17.7	20.5	-	-	-	0.5	55.8	
C-B-Co #1	Mineral matter	-	-	7.4	4.9	14.1	1.2	-	-	14.3	41.5	Cu = 16.7
	Mineral matter (large area scan)	-	-	7.4	7.4	26.0	4.9	-	-	0.2	54.1	
	Mineral matter	-	-	7.5	9.7	25.9	0.3	-	-	-	56.6	

*Cl from mounting resin

Table 7.3. Quantitative analyses of coal/bitumen coal processing residues, generated by Raylo Chemicals

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #4	Fine-grained o.a. semicoke	-	-	9.1	8.4	21.5	11.4	-	-	-	49.7	These analyses are on coal derived material
	Fine-grained o.a. semicoke	-	-	8.5	9.1	25.9	-	-	-	-	56.6	
	Fine-grained o.a. semicoke	-	-	11.5	-	31.4	-	-	-	-	57.2	" "
	Isotropic vitrinite	-	-	9.0	6.2	26.5	-	-	-	2.9	55.5	

o.a. semicoke = optically anisotropic semicoke

*Cl from mounting resin

Table 7.4. Quantitative elemental analyses of coal/bitumen residue generated by Raylo Chemicals Ltd.

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #4	Coarse-grained o.a. semicoke	-	-	4.5	2.7	34.4	-	-	-	-	58.5	These analyses are on bitumen derived material
	Coarse-flow o.a. semicoke	-	-	5.6	3.4	32.9	-	-	-	-	58.1	
	Coarse-flow o.a. semicoke	-	-	7.1	-	34.7	-	-	-	-	58.2	
	Coarse-grained o.a. semicoke	-	-	7.1	-	34.7	-	-	-	-	58.2	" "

o.a. semicoke = optically anisotropic semicoke

*Cl from mounting resin

Table 7.5. Quantitative elemental analyses of coal/bitumen residue generated by Raylo Chemicals Ltd.

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
RS 170582	Vitrinite	-	-	6.1	9.1	25.3	5.2	-	-	0.6	53.8	
	Vitrinite	-	-	5.5	9.1	25.7	5.1	-	-	0.5	54.0	
	Vitrinite	-	-	5.8	8.8	25.8	4.1	-	0.5	0.8	54.2	
R 190582	Vitrinite	10.4	10.0	10.4	10.4	10.4	-	-	-	1.5	47.1	Toluene extracted
	Vitrinite	11.1	10.2	11.1	7.9	11.1	-	-	-	1.9	46.7	
	Vitrinite	10.9	9.5	10.8	9.1	10.9	-	-	-	2.2	46.8	
R 011281-3	Vitrinite(?)	-	-	11.9	35.2	-	-	1.8	-	-	51.1	
R 221081	Vitrinite	-	-	8.1	7.9	22.9	7.0	-	1.5	1.3	51.4	
R 051181	Vitrinite	10.9	8.3	10.4	9.7	10.8	3.0	0.5	0.5	0.2	46.0	

R = distillation residue RS = reactor sample *Cl from mounting resin

Table 7.6. Quantitative elemental analyses of distillation residues and reactor samples from coal-oil processing, generated by Canmet

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
R 190582	Inertinite	-	-	10.0	9.1	19.0	7.9	-	4.0	0.5	49.5	Toluene extracted
	Inertinite	-	-	9.6	9.3	19.0	8.0	-	4.3	0.4	49.4	
RS 170582	Matrix	-	-	5.5	8.4	26.4	3.2	-	0.4	1.5	54.6	
RO11281-3	Matrix	-	-	18.7	30.2	-	-	-	-	-	51.1	
R 221081	Matrix	-	-	9.9	9.0	18.0	15.3	-	1.2	-	46.5	
	Matrix	-	-	8.5	7.9	22.9	6.7	-	1.2	1.2	51.7	
R 051181	Matrix	-	-	7.9	8.3	21.8	6.2	1.5	2.9	0.7	50.7	
RS 170582	o.a.s. from vitrinite	-	-	6.6	8.1	25.4	5.7	-	-	0.8	53.4	Vitrinite derived residues
	Vesicular, o.a.s. in matrix	-	-	7.0	9.0	25.4	3.4	-	-	0.5	54.7	

R = distillation residue   RS = reactor sample   *Cl from mounting resin

o.a.s. = optically anisotropic semicoke

Table 7.7. Quantitative elemental analyses of distillation residues and reactor samples from coal-oil coprocessing, generated by Canmet

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
R 051181	Coarse grained o.a.s. matrix	12.2	8.3	10.1	6.3	12.3	4.1	0.9	0.8	0.2	44.8	These are matrix derived semicokes
	Coarse grained o.a.s. matrix	9.7	5.5	9.1	9.7	9.7	6.3	1.9	4.1	0.9	43.1	
	Coarse grained o.a.s. matrix	10.9	6.3	8.6	7.0	9.3	10.7	3.4	3.7	0.3	39.8	" "
	Mesophase	-	-	6.0	3.6	4.6	-	-	-	54.0	31.8	
	Mesophase & isotropic matrix (l.a.s.)	-	-	9.9	7.7	21.4	10.1	1.0	-	-	49.8	
R 190582	Mineral Matter	-	-	8.1	28.1	8.3	1.9	-	0.9	0.5	52.2	Toluene extracted
	Mineral Matter	-	-	12.0	25.9	6.9	-	2.4	0.7	0.6	51.5	
	Mineral Matter	-	-	7.1	17.5	17.5	-	1.3	2.0	0.8	53.8	
R 221081	Mounting Resin	-	-	-	-	-	100.0	-	-	-	-	

R = distillation residue   Rs = reactor sample   *Cl from mounting resin

o.a.s. = optically anisotropic semicoke

l.a.s. = large area scan

Table 7.8. Quantitative elemental analyses of distillation residues and reactor samples from coal-oil coprocessing, generated by Canmet

are noted in the third column. The trace elements sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), sulphur (S), chlorine (cl), potassium (K), calcium (Ca) and iron (Fe) are referred to by the chemical symbols only. The balance, one hundred per cent less the cumulative percentage of trace elements in each sample, is assumed to be carbon (C), oxygen (O), hydrogen (H) and nitrogen (N). Analysis of the 'background' epoxy mounting resin indicates chlorine (Cl) as the only major trace element (Table 7.8). When chlorine appears in the trace element spectra of petrographically selected components it is considered to be a constituent of the mounting resin.

Quantitative trace element analyses of the feedstocks and coal-bitumen coprocessing residues generated by Raylo Chemicals are given in Tables 7.1 to 7.5. The data are grouped according to the nature of the petrographically identified component which facilitates comparisons between samples. In Appendix E, the data are grouped according to the sample number. The results of trace element analyses of the Canmet reactor sample and distillation residues are given in Tables 7.6 to 7.8 and the data are classified according to petrographically similar components.

7.21. Trace element analyses of feedstocks and residues from coal-bitumen coprocessing, generated by Raylo Chemicals Ltd. (26SQ.23440-2-9069-0,-1,-2,-3,-4)

Various optically isotropic and anisotropic components of residues from coal, bitumen, and coal-bitumen hydrogenation experiments can be identified by petrographic methods. These are described in Chapter 3. Isotropic vitrinites, inertinite and fine, medium and coarse grained, mosaic textured, anisotropic semicokes are identified in the residue from coal hydrogenation (C-B-Co-3). Isotropic bitumen, mesophase, coarse and flow textured semicokes are generated by bitumen hydrogenation, (C-B-Co-2). The coal derived solid products (C-B-Co-4)from the hydrogenation of a mixture of coal and bitumen, are principally isotropic vitrinites and fine grained, mosaic textured semicokes which can be distinguished from the bitumen derived solids by petrographic methods. The latter resemble the solid products of hydrogenated bitumen. There is one type of residual component which is common to all three residues, ie. C-B-Co-2, -3 and -4; it is coarse grained mosaic textured semicoke. This makes it difficult to identify its origin when it occurs in the coal-bitumen residue (C-B-Co-4), and it constitutes 12% of the sample. The petrographic evidence suggests that it forms from bitumen derived material. Trace element analyses were conducted to investigate this.

Trace element analyses of the possible precursor of the coarse grained, mosaic textured anisotropic semicoke, (isotropic vitrinite in C.-B.Co-0, and C-B-Co-3 and isotropic bitumen in C-B-Co-2) and analyses of mineral matter and other optically anisotropic semicokes were carried out. The results are given in Tables 7.1 to 7.5. The vitrinites in the feed coal (C-B-Co-0), the coal derived residue (C-B-Co-3), and all of the vitrinite derived semicokes in the hydrogenated coal products (C-B-Co-3) have similar trace element compositions. The major trace elements are Al, Si, S, Cl (mounting resin), Fe, and the C, H, N, O composition ranges from 48.8% to 53.5%, (Tables 7.1 and 7.2). Incidentally, the same major elements are present in the inertinite macerals and the relative percentages are also similar to the vitrinites (Table 7.1).

The bitumen derived semicokes (C-B-Co-2) contain Si, S and Cl (mounting resin). They do not contain Al or Fe (Table 7.2) and the relative percentage of S (32%) is considerably higher than in the vitrinites or vitrinite derived semicokes (20.3% to 25.9%, Table 7.2 and 7.3). The absence of Al and the high S concentration could therefore be considered characteristic of the bitumen.

In the coal-bitumen coprocessing residue (C-B-Co-4) the trace element analyses of the petrographically identified coal derived constituents, namely the fine-grained, mosaic textured semicokes (Table 7.4), produce similar results to the hydrogenated coal derived solids of C-B-Co-3. The trace element contents of the bitumen-derived semicokes (coarse, mosaic textured, anisotropic semicokes) include Al but they have high S contents (32.9% to 34.7%, Table 7.5) which distinguish them from the coal derived constituents.

It is concluded that trace element spectra, but more importantly, quantitative trace element analyses can be used to support petrographic inferences regarding the origin of semicokes in residues from the coprocessing of coals and bitumen. In this case the spectra from coals and bitumen derived solids are similar but the bitumen-derived solids can be identified by a higher S content.

7.22. Trace element analyses of reactor samples and solid distillation products from coal-oil coprocessing experments conducted by Canmet.

The reactor samples and the distillation residues generated by coprocessing coal and oil mixtures under various experimental conditions, all contain coal derived particles that can be identified petrographically (isotropic vitrinite and inertinite). The principal constituent, however, is an optically isotropic, weakly reflecting, bituminous material. It is referred to as 'bituminous matrix' because it hosts coaly particles and mineral matter (Plates 8 and 9). This bituminous residue may be residual from the vitrinite, or it may be an intermediate product of liquefaction such as asphaltenes and preasphaltenes (although it is only slightly soluble in toluene), or it may be a solid product of the bitumen. Trace element analyses of coaly particles, mineral matter and bituminous matrix were conducted to see if the origin of the bituminous matrix could be identified by the inorganic component. The results are tabulated in Tables 7.6 to 7.8.

The vitrinite in the reactor sample 170582 (Table 7.6) contains Al, Si, S, Cl (mounting resin), minor Fe and Ca; the C,H,N,O, component ranges from 53.8% to 54.2%. The same elements are present in vitrinite in the distillation residues, in some cases (190582m 051181) with the addition of K, Na, and Mg and the C,H,N,O, concentrations are around 51%. When Na and Mg are present they occur in significantly large quantities but the S content of the vitrinite is correspondingly lower (approximately 25% versus 10% to 11%).

The anisotropic semicokes in the distillation residues were thought to be derived from vitrinite (170582; Table 7.7). They have trace element contents that closely resemble the isotropic vitrinite in the reactor samples. The coarse-grained, mosaic-textured semicoke that forms from the bituminous matrix in sample 051181, contains Na and Mg and has a significantly lower S content than the vitrinites (12.3% to 9.3%).

Within the same sample, whether it is a reactor sample or a distillation residue, the relative percentages of the elements are similar for each petrographically identified species eg. vitrinite or bituminous matrix. However, there are considerable variations in the elemental concentrations of individual species from sample to sample. This makes it difficult to characterise any particular component with regard to its inorganic constituents. Consequently, no significant conclusions can be drawn from trace element analyses in this case.

7.3. Conclusions

Trace element analysis of petrographically selected components proved to be a useful method of analysing the solid residues from coal-bitumen coprocessing experiments conducted by Raylo Chemicals Ltd. The results showed reasonably good agreement with the petrographic analysis. It was found the coal derived solids could be characterised by Al, Si, S and Fe. Some bitumen derived solids lacked Al and Fe, otherwise the trace element spectra were similar and characterised by significantly higher S contents than the coal derived solids. The high S content of the coarse grained mosaic textured semicoke in the solid residue from hydrogenation of a coal-bitumen mixture suggested that it originated from the bitumen.

The inorganic elemental compositions of reactor samples and solid distillation products of coal-oil coprocessing generated by Canmet, were not consistent enough to provide useful data.

CHAPTER 8

GENERAL CONCLUSIONS AND DISCUSSION

8.1. General remarks

The samples analysed petrographically under D.S.S. Contract OSU81-000105 can be divided into three categories:

1. Feedstocks for coal liquefaction or coal-bitumen coprocessing experiments.
2. Residues from various coal liquefaction processes:
   (i) Extraction of coal derived liquids by supercritical gases
   (ii) Coal-bitumen coprocessing experiments
3. Residues from the aforementioned processes, generated under various experimental conditions.

With these categories in mind, we can review the results of the petrographic analyses, reported in Chapters 3 to 7, in the following manner:

1. The effects of petrographic composition and rank of the coal feedstocks on coal liquid yields.
2. The variable nature of the solid residues generated from various liquefaction processes and their net effects upon coal liquid yields.
3. Variations in the nature of the solid residues due to variations in experimental conditions employed during individual liquefaction processes.

8.2. The effects of petrographic composition of the coal feedstocks on coal liquid yields

Various authors have demonstrated the effects of the petrographic composition and rank of the coal feedstocks upon the percentage conversion or on coal liquid yields during hydrogenation of coal. Given, et al. (1975), noted that high volatile bituminous coals gave better conversions than lower rank coals, especially those with high mineral matter contents. They also observed fair correlation between conversion and the concentration of reactive macerals (vitrinite and sporinite). Guyot, 1978 and 1979, detected a direct relationship between the rank and petrographic composition (Petrofactor) of some Australian coals and conversion, and Diessel and Guyot 1979, showed that inertinite macerals with a reflectance, R_0 max, of less than 1.4% were reactive during coal hydrogenation.

Previous studies on low rank Canadian coals by the the Energy Research Unit, have not yielded any direct relationships between coal conversion and petrographic composition and coal rank for two reasons. Firstly, the results of the petrographic studies of coal feedstocks from coal liquefaction experiments conducted by most of the Canmet contractors could not be correlated with conversion data because the results of the experiments were confidential. Secondly, when the results of the coal liquefaction experiments were made available for correlation with petrographic data, the experiments were either conducted under variable experimental conditions or they resulted from coprocessing of coal and oils or bitumen. The products were not derived entirely from coal and therefore the effects of coal composition could not be detected. Nevertheless, the influence of petrographic composition and rank of the feedstock is considered to have significant affects on the liquefaction potential.

8.21. The coal feedstocks examined in this study, i.e. the high volatile bituminous coals (NSRFC) which are discussed in Chapter 4, and the lignite (SRC) described in Chapter 5, are all suitable feedstocks for coal liquefaction. The Prince and Lingan Mine coals from Nova Scotia are high volatile bituminous coals of similar rank. The percentage of reactive macerals varies from 86.3% to 91.6%, which favours relatively good conversion. The lignite from Saskatchewan (SRC) contains 87.2% reactive macerals of which two thirds comprises structured huminite macerals. In previous studies on liquefaction of lignites, (Energy Research Unit, 1981) the structured huminites were found to be particularly reactive. This coal should therefore be most suitable for coal liquefaction, despite its low rank.

To further studies of petrographic compositions of Canadian coals and their effects on coal liquid yields, it is suggested that coal liquefaction experiments, using coals of variable composition and rank, be carried out under identical experimental conditions so that relationships between petrographic character of feed coals and conversion can be investigated more thoroughly. In addition, more information on the liquefaction potential of individual coal macerals or maceral groups would contribute to our understanding of the liquefaction process, and facilitate assessment of the overall liquefaction potential of a given coal. Fundamental research of this kind would greatly benefit the application of coal petrology to coal liquefaction and possibly enhance the development of coal liquefaction technology.

8.3. The nature of the solid residues from various coal liquefaction processes and their effects upon liquid yields

The formation of insoluble, optically anisotropic semicokes in the solid residues from coal liquefaction processes is known to cause technological problems, such as reactor fouling and it occurs at the expense of high coal liquid yields. It is therefore desireable to minimise the amount of semicoke that forms, either in the reactor or during distillation of the products, by controlling the experimental conditions. Semicokes are known to form from vitrinite in coals, from the liquid products and from intermediate compounds, under hydrogen deficient condition (Shibaoka and Ueda, 1978). During the coprocessing of coals and bitumens, semicoke forms primarily from bituminous products such as asphaltenes and preasphaltenes, and from an insoluble bituminous material at temperatures over 380°C, (Energy Research Unit, 1982). Optically anisotropic semicokes can only be detected by microscopical examination of solid residues. The amount and type of semicoke can also be assessed only by petrographic methods.

To detect semicokes in the solid residues from coal liquefaction is the first step towards preventing its formation. Supercritical gas extraction of coals generally produces optically isotropic chars and very little or no optically anisotropic semicokes (Energy Research Unit, 1981, 1982). Supercritical toluene extraction of vitrinite rich, Nova Scotia coals of high volatile bituminous A and C ranks produces mixed isotropic coal chars with substantial amounts of anisotropic semicoke (66% and 45%, respectively). The higher ranking coal (sub-bituminous A) produces more anisotropic semicoke at 3.8 mPa (2000 psig) and 450°C. Under these conditions it is therefore more desirable to use low rank coals for supercritical toluene extraction in order to minimise the formation of anisotropic semicoke in the insoluble residue.

8.31. Residues from sub-bituminous coal, bitumen and coal-bitumen hydrogenation at 450°C, (Chapter 3) also contain large amounts of optically anisotropic semicokes (99%, 93.4% and 57.4%, respectively).

However, semicoke formation from vitrinite in the sub-bituminous coal, is substantially reduced by coprocessing coal and bitumen. The coal derived portion of the coal-bitumen residue amounts to 74.2% of the total solid product. Less than half of it (32.2%) is anisotropic semicoke. This, together with the fine grain size of the anisotropic mosaic and the relative abundance of isotropic coal derived solids present, indicates that the process of forming optically anisotropic semicokes is severely retarded by the addition of bitumen to coal. The presence of coal in the mixture does not, however, appear to retard semicoke formation in the bitumen derived solids.

8.32. The reactor samples and the solid distillation products from coal-oil coprocessing experiments conducted under slightly variable standard temperatures, pressures, residence times and coal concentrations (Chapter 6) are dominantly optically isotropic residues of a bituminous nature which are slightly soluble in toluene. The relative concentrations of coal derived solids and intermediate bituminous products vary with the experimental conditions.

It is significant that the different coal liquefaction processes produce petrographically different residues with respect to the optical character of the solid products. Unfortunately, neither conversion nor liquid yield data are available for correlation with the results of the petrographic analyses.

8.4. Variations in the experimental conditions and the effects upon the nature of the residues from coal-bitumen coprocessing

Previous studies of the solid products and reactor samples from coal-bitumen coprocessing experiments conducted at high temperatures

(430°C) showed that the solid residues were bituminous materials, derived largely from bitumen, from which large amounts of optically anisotropic semicoke had formed, (Energy Research Unit 1982). The solid products collected from the reactor and the solids produced by distillation of the end products from coal-bitumen coprocessing conducted at set (standard) experimental conditions, are principally isotropic bituminous materials with some upgraded coal (vitrinite) particles (Chapter 6). The experimental variable that most affects the character of the distillation residues is reaction temperature. At various reaction temperatures (t-50, t-25, t, t +25), neither the morphology of the residual constituents nor the relative percentages of anisotropic semicoke are significantly altered, but upgrading of vitrinitic coal particles occurs. The degree of upgrading, with respect to carbon contents, as indicated by the reflectance, increases as the reaction temperature increases.

The reactor contents are mostly isotropic solids derived principally from the bitumen or oil. They do not change significantly as a result of varying the operating conditions except when the coal concentration in the coal-bitumen feed mixture is altered. When the standard coal concentration is halved, the amount of coal in the reactor sample is approximately halved.

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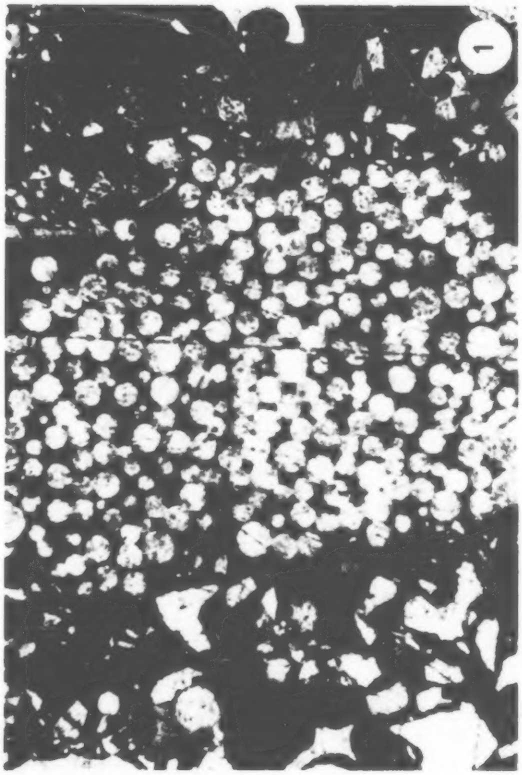
Plate 1	Mesophase spherules in weakly reflecting isotropic bitumen. Raylo C-B-Co-2 (x500, 1/2 x N)
Plate 2	Coarse-grained, mosaic textured semicoke from bitumen. Raylo C-B-Co-2 (x500, 1/2 x N)
Plate 3	Flow-textured semicoke from bitumen. Raylo C-B-Co-2 (x500, 1/2 x N)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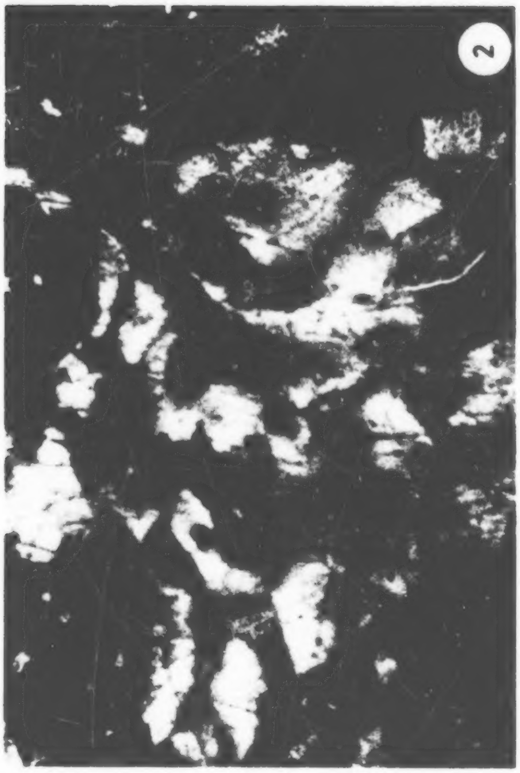
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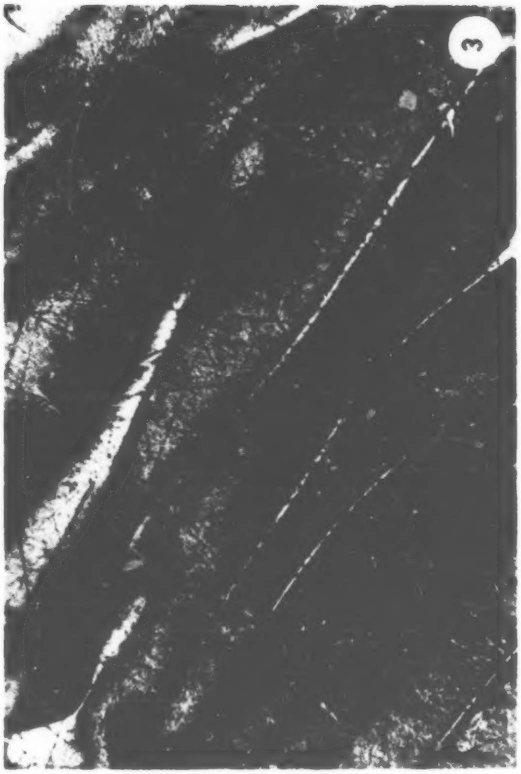
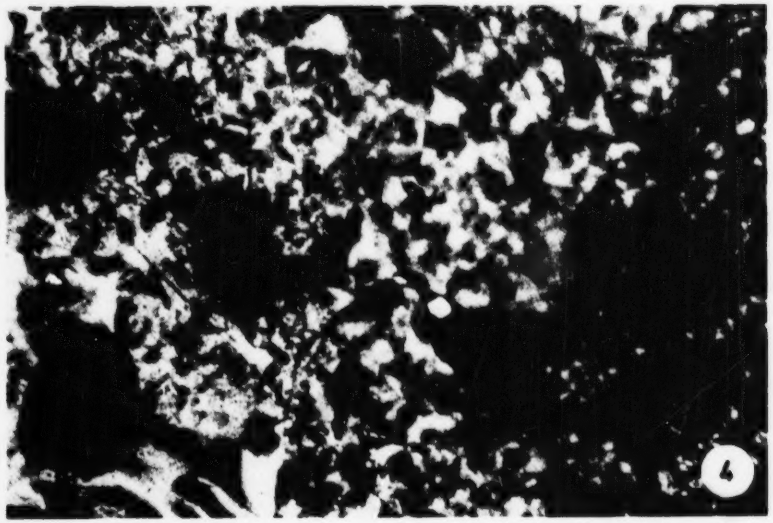

③

Plate 4	Fine grained, mosaic-textured semicoke from vitrinite. Raylo C-B-Co-3 (x500, 1/2 x N)
Plate 5	Coarse grained, mosaic-textured semicokes from vitrinite. Raylo C-B-Co-3 (x500, 1/2 x N)
Plate 6	Anisotropic vitroplast with fine-grained mosaic texture. Raylo C-B-Co-3 (x500, 1/2 x N)



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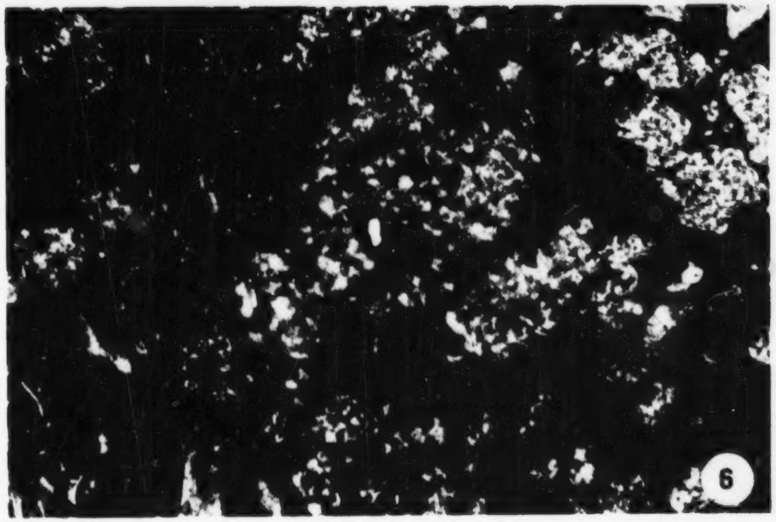

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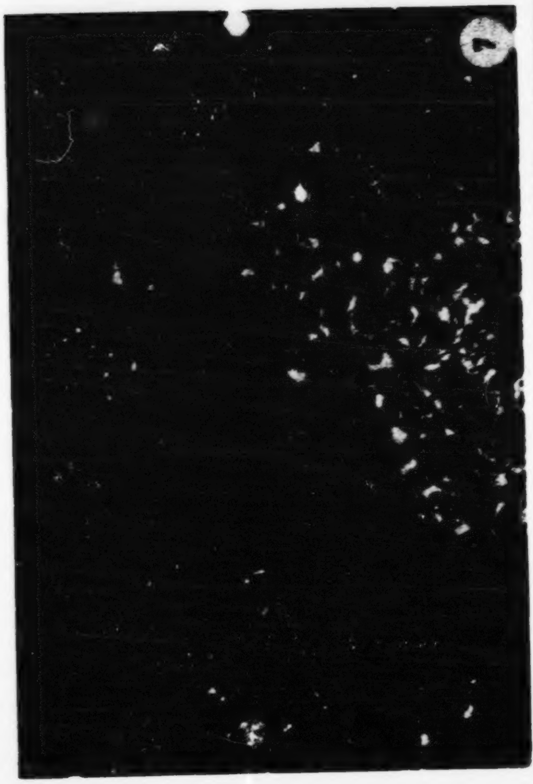
Plate 7	Isotropic vitrinite (centre, top), isotropic vitrinite with anisotropic rim (centre left) and anisotropic mosaic textured semicoke from bitumen (centre bottom). Raylo C-B-Co-4 (x500, 1/2 x N)
Plate 8	Isotropic bituminous matrix (b) with vitrinite char particles (v) embedded in it. Canmet reactor sample 030282 (x500, 1/2 x N)
Plate 9	Isotropic bituminous matrix (b) vitrinite particles (v) and catalyst (c). Canmet distillation residue 241181 (x500, PPL)



APPENDIX A

Petrographic analyses of liquefaction feedstocks and residues, Raylo Chemicals Ltd.

PETROGRAPHIC ANALYSIS OF COAL FEEDSTOCK FOR SUPERCRITICAL TOLUENE EXTRACTION OF COAL
(26 SQ.23440-2-9098-STE 205-1-A)

Maceral, %	(Nova Scotia 1)
Vitrinites:	
Vitrinite A	49.6
Vitrinite B	30.8
Inertinites:	
Fusinite	4.4
Semifusinite	3.8
Macrinite	0.6
Micrinite	0.8
Inertodetrinite	2.8
Liptinites:	
Sporinite	5.0
Resinite	0.2
Cutinite	0.4
Liptodetrinite	0.6
Mineral Matter:	
Pyrite	1.0
	100%
Summary:	
Total Vitrinite	80.4
Total Inertinite	12.4
Total Liptinite	6.2
Total Mineral Matter	1.0
% Reflectance, R_0AV:	
Vitrinite A =	0.79%
Vitrinite B =	0.63%

Notes:

- This is a vitrinite rich (80.4%), high volatile bituminous coal.
- Fusinite (4.4%) and semifusinite (3.8%) are the dominant inertinite macerals.
- Sporinite (5.0%) is the major liptinite maceral; it flouresces orange brown in blue violet light.
- The reflectance (R_0AV) is higher than that of Coal 2, which suggests a marked difference in rank.

Raylo Chemicals Ltd.

Appendix A-2

PETROGRAPHIC ANALYSIS OF COAL FEEDSTOCK FOR SUPERCRITICAL TOLUENE EXTRACTION OF COAL
(26 SQ.23440-2-9098-STE 205-1-B)

Contents	(Nova Scotia 2)
Vitrinites:	
Vitrinite A	43.6
Vitrinite B	37.0
Liptinites	
Resinite	0.4
Cutinitenite	0.6
Sporinite	2.6
Liptodetrinite	0.6
Inertinites	
Fusinite	8.0
Semifusinite	3.2
Macrinite	0.2
Semimacrinite	1.4
Sclerotinite	0.2
Inertodetrinite	1.2
Mineral Matter:	1.0
	100%
Summary:	
Total Vitrinite	80.6
Total Liptinite	4.2
Total Inertinite	14.2
Total Mineral Matter	1.0
% Reflectance, R_0AV:	0.59 %
Std. deviation =	0.08 %
Variance =	0.007%

Comments:

- A slightly higher inertinite content than coal 1 suggests that coal 2 will probably have a slightly higher ash content and better heating value, otherwise the two coals are similar in petrographic composition.
- The reflectance of coal 2 is much less than that of coal 1; this would indicate a lower rank coal

Appendix A-3

Comparison of chars from coals 1 and 2

Features common to both coals are:

- They contain isotropic vitrinite char and anisotropic vitrinite-derived semicokes; both of these are vesicular.
- The anisotropic semicoke occurs as ultrafine to fine-grained granular-textured mosaics.
- The mineral matter content is low.
- The reflectance of the isotropic vitrinite char is similar.

The chars differ from one another in the following ways:

- The relative amounts of isotropic vitrinite and anisotropic material; char from coal 1 is dominantly anisotropic semicoke (66.4%), while the char from coal 2 comprises equal amounts of isotropic vitrinite char (45.2%) and anisotropic semicoke (45.0%)
- Liptinite is present in the char from coal 1.

Raylo Chemicals Ltd.

Appendix A-4

PETROGRAPHIC ANALYSIS OF COAL CHAR FROM SUPERCRITICAL TOLUENE EXTRACTION
(26 SQ.23440-2-9098-STE 205-1-15)

Contents	(supercritical toluene extracted char from coal 1)
	%
Isotropic vitrinite	23.4
Anisotropic vitrinite	
- ultrafine grained mosaic coke	17.2
- fine-grained mosaic coke	49.2
Inertinite - fusinite	3.0
- semifusinite	2.4
- macrinite	0.4
- inertodetrinite	1.6
Liptinite - sporinite	1.0
- resinite	0.2
- liptodetrinite	0.2
Mineral Matter:	1.4
	100%
Summary:	
Total Isotropic vitrinite	23.4
Total Anisotropic vitrinite	66.4
Total Inertinite	7.4
Total Liptinite	1.4
Total Mineral Matter	1.4

% Reflectance, ($R_o$random, isotropic vitrinite) = 0.85%

Notes:

- The dominant component is vitrinite-derived anisotropic semicoke which has an ultrafine-grained granular mosaic texture.
- Extensive vesiculation and some softening of both anisotropic and isotropic vitrinite particles occurs.
- Despite reaction at 400°C and 2000 psig, liptinite is present.
- Most liptinites fluoresces an orange to brown colour when illuminated with blue violet light. The liptinites in the feedstock do likewise.
- Some liptinites, visible in incident light, do not fluoresce.
- The mineral matter (1.4%) is metallic, likely pyrite.

Raylo Chemicals Ltd.

Appendix A-5

PETROGRAPHIC ANALYSIS OF COAL CHAR FROM SUPERCRITICAL TOLUENE EXTRACTION OF COAL
(26 SQ.23440-2-9098-STE 205-3)

Contents	(supercritical toluene extracted char Nova Scotia coal 2) %
Isotropic vitrinite	45.2
Anisotropic vitrinite	
- ultrafine grained mosaic coke	19.2
- fine grained mosaic coke	25.8
Inertinite - fusinite	1.6
- semifusinite	3.4
- macrinite	0.2
- semimacrinite	0.4
- inertodetrinite	3.2
Mineral Matter:	1.0
	100%
Summary:	
Total Isotropic vitrinite	45.2
Total Anisotropic vitrinite	45.0
Total Inertinite	8.8
Total Mineral Matter	1.0

% Reflectance (R_0 random isotropic vitrinite) = 0.87%

Notes:

- The dominant components are isotropic vitrinite char (45.2%) and anisotropic semicoke (45.0%) which is a vitrinite-derived and ultrafine to fine grained granular mosaic-textured.
- Both isotropic char and anisotropic semicoke contain vesicules ranging from <10 μm to >100 μm.
- Liptinite is not present in this char.
- There are minor amounts of metallic mineral matter, likely pyrite.

Raylo Chemicals Ltd.

Appendix A-6

PETROGRAPHIC ANALYSIS OF FEEDSTOCK FOR COAL-BITUMEN COPROCESSING
(26 SQ.23440-2-9069-0)

Raylo C-B-Co 0 (Coal)

Contents	%
Vitrinite:	
Structured	74.1
Groundmass	15.0
Unstructured	2.9
Vitrinite fines	2.4
Liptinite:	
Sporinite	1.3
Liptodetrinite	0.7
Inertinite:	
Fusinite	0.7
Semifusinite	0.8
Inertodetrinite	1.4
Mineral Matter	
- pyrite	0.7
- other (clays	-
	100%
Summary:	
Total Vitrinite	94.4
Total Liptinite	2.0
Total Inertinite	2.9
Total Mineral Matter	0.7
	100%

% Reflectance:

Mean R_0 random	0.42%

Notes:

- This is vitrinite rich, sub-bituminous coal (94.4% vitrinite) contains minor amounts of liptinite (2%, spores dominant) and inertinite (2.9%).

Raylo Chemicals Ltd. Appendix A-7

PETROGRAPHIC ANALYSIS OF FEEDSTOCK FOR COAL-BITUMEN COPROCESSING
(26 SQ.23440-2-9069-1)

Raylo C-B-Co 1 (Altered coal)

Contents:	%	
Vitrinite derived components:		
Isotropic char	86.6	99.4%
Degraded isotropic char	9.8	
Softened/vitroplast	0.2	
Anisotropic semicoke (fine grained mosaic)	2.8	
Inertinite	0.4	
Mineral (excluding catalyst)	0.2	
	100%	
% Reflectance, Mean R_0 random (vitrinite char)	1.67%	

Notes:

- Dominantly isotropic char from vitrinite with a reflectance equivalent to a low volatile bituminous coal (approx. 18% volatile matter)
- Minor amounts of char occur in a degraded form and this has a tendency to form anisotropic semicoke with a fine-grained mosaic texture.
- Occassionally the isotropic char exhibits rounding and softening, producing dispersions of minute vitroplast globules ($< 5\,\mu m$).
- Inertinite fragments and mineral matter (apart from catalyst) are rare.
- Liptinite macerals are absent

Comments: main effects of heating with anthracene.

- The main effects of heating with anthracene at 400°C and 2000 psi are: (i) vitrinite produce an isotropic char similar to a low volatile bituminous coal and (ii) complete reaction of liptinite macerals.
- There is no observed relationship between concentration/presence of catalyst and the nature of the residual components.

Raylo Chemicals Ltd. Appendix A-8

PETROGRAPHIC ANALYSIS OF RESIDUE FROM BITUMEN LIQUEFACTION
(26 SQ.23440-2-9069-2)

Raylo C-B-Co 2 (Bitumen coke)

Contents:	%	
Isotropic matrix	6.6	
Anisotropic semicoke:		
Mesophase spheres	1.2	93.4
Coarse mosaic	32.4	
Coarse-flow type	26.2	
Flow type	3.4	
Fine mosaic	0.2	
Anisotropic fines	30.0	
Mineral Matter	-	
	100%	

Reflectance - R_0 isotropic matrix	0.42%
- mosaic R_{max}	2.3%
R_{min}	1.35%

Notes

There are two dominant constituents of the bitumen residue: (i) aggregates (up to 500 μm) of anisotropic fines (<50 μm) and (ii) particles (up to 800 μm) of coarse to flow-textured anisotropic semicoke. Both species have formed from isotropic bitumen. The aggregates form a fine to medium grained, mosaic-textured semicoke that divides the isotropic matrix into small angular fines. The coarse to flow-textured semicoke forms by development, growth and coalescence of mesophase spherules. This is accompanied by shrinkage of the isotropic matrix producing concentrically fractured matrix (shrinkage fractures). The resultant semicoke is commonly vesicular when in a coarse mosaic form; the coarse flow type, which dominates, forms larger angular particles up to 600-800 μm (the edges of particles are dictated by flow texture).

Raylo Chemicals Ltd.

Appendix A-9

PETROGRAPHIC ANALYSIS OF RESIDUE FROM COAL LIQUEFACTION
(26 SQ.23440-2-9069-3)

Raylo C-B-Co 3 (Coal coke)

Contents:

	%	
Isotropic vitrinite	-	
Isotropic vitroplast	1.0	
Anisotropic vitroplast		
- Fine mosaic semicoke	59.2	99.0%
- Medium grained semicoke	13.6	
- Coarse grained semicoke	25.2	
- Coarse flow type semicoke	1.0	
	100%	

Reflectance:

R_oAV vitroplast	0.43%
R_oAV vitrinite	0.66%
$R_o$max coarse mosaic coke	2.45%
$R_o$min coarse mosaic coke	1.47%
Bireflectance mosaic coke	0.94%

Notes:

- Ninety nine per cent of the residue comprises anisotropic semicoke produced from vitroplast.
- The dominant type is fine to medium-grained, mosaic textured semicoke.
- The fine granular mosaics occur in the centres of particles and medium grained mosaics occur on the peripheries of vitroplast globules; they range from 10-60 microns diameter and coalesce, forming particles up to 1000 μm which are commonly vesicular.
- Further coalescence of anisotropic vitroplast produces coarse grained mosaic semicoke particles, greater than 300 μm diameter with rounded margins, some of which have become vesicular and resemble bitumen semicoke with coarse-flow textured anisotropy.
- No mesophase was observed but occasionally a finely disposed anisotropic globular residue was observed.

Raylo Chemicals Ltd.

Appendix A-10

PETROGRAPHIC ANALYSIS OF RESIDUE FROM COAL-BITUMEN COPROCESSING (26 SQ.23440-2-9069-4)

Raylo C-B-Co 4 (Coal/bitumen coke).

Contents:

	%
Isotropic - vitrinite	41.6
- inertinite	0.4
Anisotropic-vitroplast (medium)	1.0
Ultrafine-fine-medium grained mosaic coke	31.2
Isotropic - bitumen	0.6
Anistropic-mesophase	0.8
- coarse grained mosaic coke	11.8
- coarse flow textured coke	9.8
- fines	2.8
	100%

Coal derived solids:	
- isotropic	42.0
- anisotropic semicoke	32.2
	74.2%
Bitumen derived solids:	
- isotropic	0.6
- anisotropic semicoke:	25.2
	25.8%

Totals:

- Total % isotropic residue	46.2%
- Total % anisotropic	57.4%

Reflectance:

R_0 random isotropic vitrinite	1.6%
R_0 random anisotropic vitrinite	2.28%
R_0AV isotropic bitumen	2.4%
R_0max anisotropic bitumen	2.4%

Notes:

- The dominant constituents are coal-derived solids (74.2%) comprising particles 50 μm or so in diameter.
- The majority are isotropic with narrow (< 1 μm) anisotropic rims of ultrafine to fine grained mosaic coke.
- They are vitrinite-derived coke exhibiting a higher reflectance than the feed coal vitrinite.
- Occassionally they contain inertinite but not liptinite macerals. Some exhibit anisotropic ultrafine-grained mosaic texture.
- The coal derived particles appear to be derived from large particles (up to 400 μm long) by shrinkage of the anisotropic areas that once held them together. Medium grained matrix semicoke appears to form from vitroplast (1%).
- The remainder of the residue (26%) comprises coarse to coarse-flow and flow type semicokes derived from bitumen, and minor amounts of isotropic bitumen with mesophase, lower reflectance than the vitrinite, shrinkage cracks and vesicules.

Comments:

- The presence of both coal and bitumen mutually alters the optical textures of the solid residues from each.
- There is less tendency for vitroplast and semicoke to form in the vitrinitic residue.
- Only one quarter of the residue is derived from bitumen.

APPENDIX B

Petrographic analyses of coal liquefaction feedstocks

Nova Scotia Resarch Foundation Corporation

Nova Scotia Research Foundation Corporation

Appendix B-1

PETROGRAPHIC ANALYSES OF COAL LIQUEFACTION FEEDSTOCKS
(D.S.S. Contract No. OSQ81-00039)

Maceral, %	Prince "C"	Prince "D"
Vitrinites:		
Vitrinite A	46.2	45.6
Vitrinite B	33.6	34.0
Liptinites:		
Resinite	0.6	---
Cutinite	1.0	0.2
Sporinite	6.0	5.2
Liptodetrinite	0.4	0.4
Inertinites:		
Fusinite	5.2	7.6
Semifusinite	2.4	2.6
Macrinite	0.2	0.2
Semimacrinite	0.2	---
Micrinite	---	---
Sclerotinite	---	---
Inertodetrinite	0.6	1.0
Mineral Matter:		
Pyrite	1.8	2.0
Other	1.8	1.2
Summary:		
Total Vitrinite	79.8	79.6
Total Liptinite	8.0	5.8
Total Inertinite	8.6	11.4
Total Mineral Matter	3.6	3.2
% Reflectance:		
Mean R_0 random	0.69	0.67
Std. Dev.	0.01	----

Nova Scotia Research Foundation Corporation

Appendix B-2

PETROGRAPHIC ANALYSES OF COAL LIQUEFACTION FEEDSTOCKS
(D.S.S Contract No. OSQ81-00039)

Maceral, %	Lingan "I"	Lingan "J"	Lingan "K"
Vitrinites:			
Vitrinite A	38.2	40.9	42.0
Vitrinite B	43.4	38.8	40.8
Liptinites:			
Resinite	0.8	0.4	-
Cutinite	0.8	0.6	1.0
Sporinite	6.6	5.1	6.4
Liptodetrinite	---	0.1	-
Inertinites:			
Fusinite	5.0	5.9	4.0
Semifusinite	2.6	2.9	4.2
Macrinite	0.4	0.9	-
Semimacrinite	0.2	0.1	0.4
Micrinite	---	---	-
Sclerotinite	---	---	-
Inertodetrinite	0.8	0.4	0.4
Mineral Matter:			
Pyrite	0.6	1.95	0.6
Other	0.6	1.95	0.2
Summary:			
Total Vitrinite	81.6	79.7	82.8
Total Liptinite	8.2	6.2	7.4
Total Inertinite	9.0	10.2	9.0
Total Mineral Matter	1.2	3.9	0.8
% Reflectance:			
Mean R_0 random	0.72	0.70	0.71
Std. Dev.	0.01	----	0.01

APPENDIX C

Petrographic analysis of coal feedstock,

Saskatchewan Research Council

Saskatchewan Research Council

Appendix C-1

PETROGRAPHIC ANALYSIS OF COAL LIQUEFACTION FEEDSTOCK
(D.S.S. Contract No. ________________)

% Macerals	%
Huminites:	
Textinite	1.4
Texto ulminite	1.8
Eu-ulminite	55.4
Densinite	22.4
Corpohuminite	4.0
Liptinites:	
Sporinite	2.6
Resinite	0.6
Liptodetrinite	2.2
Inertinites:	
Fusinite	1.8
Semifusinite	3.2
Macrinite	0.2
Sclerotinite	0.6
Inertodetrinite	1.8
Mineral Matter:	2.0
	100%

Summary:	
Total Huminite	85.0
Total Liptinite	5.4
Total Inertinite	7.6
Total Mineral Matter	2.0
	100%

% Reflectance:

Mean R_0 (random):	0.32%
Standard deviation:	0.05

PETROGRAPHIC ANALYSIS OF LIQUEFACTION FEEDSTOCK

Report on Petrographic Analysis:

1) The reflectance, R_0(Av), value on structured huminites is 0.32%.
2) The sample appears to have been oxidized. This is perhaps one of the reasons for the pitted appearance of much of the huminite material.
3) The total reactive material (huminites) in the sample is about 80%.
4) Sporinite is the dominant liptinite maceral.
5) The sample contains 2.2% mineral matter (mainly pyrites, some clay minerals).

The maceral composition in this sample is comparable to other samples from the Estevan area. The percentages of huminites, inertinites, liptinites and minerals, and the reflectance fall in the range of several other samples previously analysed from the Estevan area.

APPENDIX D

Petrographic analyses of Canmet coal/oil slurry residues, reactor samples and feed mixtures

PETROGRAPHIC ANALYSIS OF LIQUEFACTION FEEDSTOCK

(Dry) Feedstock (catalyst impregnated)

Contents

	%
Vitrinite	88.6
Inertinite	6.2
Liptinite	2.6
Mineral - Metallic	0.4
- Other	2.2
	100%

Notes

- Coal: vitrinite rich sub-bituminous (vitrinite slightly structured).
- Inertinite: fragmented, highly dispersed/detrital.
- Liptinite: spores and resins.
- Mineral matter: clay and silica and some metallic iron - probably indigenous.
- Vitrinite $R_0AV = 0.42\%$.

Comments

Mineral matter does not total same as residues. Much of it looks indigenous to coal rather than added/impregnated.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Feedmixture: 290782 (toluene extracted)

Contents

	%
Coal	100%
Bituminous Matrix	-

Petrographic composition of Coal:

Vitrinite	91.6
Inertinite	7.8
Liptinite	0.2
Mineral Matter	0.4
	100%

Reflectance

R_0AV Vitrinite	0.51%
Std. Dev.	0.04

Notes

- Particle size: fines to 100 µm particles.
- No oil exuding from residue.
- Mineral content: pyrite/marcasite and clays.
- Coal: vitrinite-rich, sub-bituminous.
- Liptinite: resins-spores.
- Inertinite: detrital.
- Mineral: mainly clays.

Comments

Toluene extracted feed, R_0AV vitrinite = 0.51%. In the dry, unextracted coal, R_0AV vitrinite = 0.41%. This suggests that solvent extraction may affect the rank of the vitrinite.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Reactor Sample: 030282 toluene insoluble residue

Contents:

	%
Remnants of isotropic bituminous matrix	63.33
Isotropic vitrinite	32.33
Isotropic inertinite	3.0
Mineral matter - metallic	1.33
- other	-
	99.99%

Notes

- No oil present
- Bituminous matrix: isotropic, occurs as particles up to 600 μm diameter, comprises very weakly reflecting, less concentrated bituminous residue mixed with sub-micron sized mineral matter.
  - contains mesophase and small anisotropic areas of fine granular mosaic textured semicoke.
  - hosts abundant coaly particles.
- Coal: appears relatively unaltered.
- Vitrinite $R_0AV = 0.55$ %.

Comments

Isotropic matrix must be fairly soluble in toluene but not the anisotropic portion. The reflectance of the vitrinite is similar to that of the vitrinite in the extracted feed mixture (290782).

CANMET

Appendix D-4

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Reactor Sample: 120582 (toluene insoluble residue)

Contents:

	%
Isotropic residual bituminous matrix	72.6
Vitrinite - isotropic	17.0
- anisotropic	0.2
Inertinite - isotropic	5.8
- anisotropic	0.2
Mineral Matter - metallic	4.2
- other	-
	100%

Notes

- No oil present
- Bituminous matrix: isotropic, occurs in weak concentrations mixed with very fine mineral forming particles up to 600 μm diameter.
    - contains mesophase spherules and medium-coarse granular mosaic-textured semicoke.
    - contains abundant coaly particles - vitrinite, inertinite and possibly micrinite.
- Vitrinite: particles exhibit variable degrees of preservation - may indicate dissolution in matrix.
- Reflectance of vitrinite particles, R_0AV = 0.55%
- Liptinites: absent.

Comments

Mesophase and anisotropic semicoke that form from isotropic bituminous matrix are insoluble in toluene, but some of the isotropic matrix is toluene soluble.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUES

Reactor Sample: 081281 toluene insoluble residue

Contents

	%
Concentrated isotropic bituminous matrix	0.7
Remnants of isotropic bituminous matrix	95.3
Vitrinite - isotropic	3.0
- anisotropic	0.3
Inertinite-isotropic	0.3
Mineral matter - metallic	0.3
	100%

Notes

- No oil present.
- Bituminous matrix: isotropic, weakly reflecting and occurs in diffuse concentrations mixed with very fine mineral matter.
  - contains coaly particles-vitrinite, inertinite.
  - reflectance = 0.47 %.
- Liptinite absent.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Reactor Sample: 190282 (No Coal)

Contents:

	%
Isotropic bituminous matrix	96.0
Anisotropic bituminous matrix	1.5
Mineral matter - metallic	1.5
- other	1.0
	100%

Notes

- Isotropic bituminous matrix: occurs as sub-rounded to sub-angular fragments up to 300 μm diameter.
  - Weakly reflecting, $R_0AV = 0.29\%$.
  - Slightly vesicular.
  - Contains mesophase and fine mosaic textured semicoke patches up to 50 μm.
  - Particles commonly have (dark) weakly reflecting rims.
  - Contains metallic and fine mineral particles (catalyst)

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 030282

Contents:

	%
Isotropic bituminous matrix	88.8
Isotropic vitrinite	3.0
inertinite	0.2
Inertinite	2.0
Mineral - metallic	4.6
- other	1.4
	100%

Notes

- Isotropic bituminous matrix: highly vesicular, weakly reflecting and contains finely disseminated, sub-micron sized mineral matter and coaly particles.
- Oil exudes from matrix.
- Reflectance of the matrix, R_0AV = 0.31%.
- Coal: vitrinite (isotropic and minor amounts of anisotropic) and inertinite particles less than 50 µm in diameter.
- Reflectance of vitrinite, R_0AV = 0.49%.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 140582

Contents:

	%
Isotropic bituminous matrix	77.6
Vitrinite - isotropic	12.4
- anistoropic	0.2
Inertinite	2.0
Mineral - metallic	4.6
- other	1.4
	100%

Notes

- Isotropic bituminous matrix: comprises weakly reflecting, isotropic, vesicular material with abundant finely disseminated sub-micron sized mineral particles and coal fragments.
- Oil exudes from matrix.
- Reflectance of the matrix, $R_0AV = 0.35\%$.
- Coal: vitrinite (isotropic and minor amounts of anisotropic) and inertinite. No liptinite.
- Reflectance of vitrinite, $R_0AV = 0.57\%$.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 011281-3

Contents:

	%
Isotropic bituminous matrix	91.2
Isotropic vitrinite	3.0
inertinite	0.6
Mineral Matter - metallic	2.2
- other	3.0
	100%

Notes

- Isotropic bituminous matrix: highly vesicular, flourescent, slightly higher reflectance than 170582, contains abundant finely disseminated mineral matter, and possibly micrinite.
- Oil exudes from matrix.
- Vitrinite: particles 50 μm and less, in various states of preservation - appears to be 'dissolving' in matrix.
- Inertinite: particles up to 50 μm.

Comments

Vitrinite possibly dissolving and contributing to matrix.

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Appendix D-10

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 221081

Contents:

	%
Isotropic bituminous matrix	94.6
Vitrinite - isotropic	4.2
- anisotropic	-
Inertinite	0.6
Mineral - metallic	0.6
- other	-
	100%

Notes

- Isotropic bituminous matrix: contains small amounts of vitrinite, inertinite and mineral.
  - Matrix is difficult to polish due to the difference in relief between the softer matrix and the coal.
  - Oil exudes from matrix.
- The reflectance (R_0AV) of the matrix is 0.26%.
- Coal: comprises isotropic and anistoropic vitrinite, and inertinite.
- The reflectance (R_0AV) of the vitrinite is 0.52%.

Comments

This sample is similar to residues 260882 and 290782.

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Appendix D-11

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 290782

Contents:

		%
Isotropic bituminous matrix		90.6
Vitrinite	- isotropic	8.0
	- anisotropic	-
Inertinite		0.6
Mineral	- metallic	0.8
	- other	-
		100%

Notes

- Isotropic bituminous matrix: hosts small amounts of coal and mineral matter.
- The matrix is difficult to polish; being extremely soft, there is a relief difference between the matrix and the coal/mineral.
- Oil exudes from matrix.
- The reflectance (R_0AV) of the matrix is 0.25%.
- Coal: comprises vitrinite (isotropic and anisotropic) and inertinite.
- The reflectance of the coal (R_0AV) is 0.57%.

Comments

This sample is similar to residues 221081 and 260882 but the reflectance of the vitrinite is greater.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 260882

Contents:

	%
Isotropic bituminous matrix	95.2
Vitrinite - isotropic	3.4
- anisotropic	-
Inertinite	0.2
Mineral - metallic	1.2
- other	-
	100%

Notes

- Isotropic bituminous matrix: contains minor amounts of vitrinite, inertinite and mineral.
  - The matrix is difficult to polish due to the relief difference between matrix and the coal.
  - Oil exudes from matrix.
- The reflectance (R_0AV) of the matrix is 0.23%.
- Coal: comprises vitrinite (isotropic and anisotropic) and inertinite.
- The reflectance of the vitrinite (R_0AV) is 0.45%.

Comments

- This sample is similar to residues 290782 and 221081.
- The reflectance of the vitrinite is less than that of the vitrinite in the feed mixture.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 271081

Contents:

	%
Isotropic bituminous matrix	92.0
Isotropic vitrinite	7.0
inertinite	-
Mineral Matter	1.0
	100%

Notes

- Bituminous matrix: isotropic, vesicular, dense, occurs as particulate matter up to 300-600 μm diameter hosts coal particles and mineral matter, commonly vesicular, flouresces under blue/violet light.
- Oil exudes from matrix.
- The reflectance of bituminous matrix (R_0AV) is 0.24%.
- Coal: particles comprise isotropic vitrinite and inertinite approximately 50 μm diameter.
- The reflectance of vitrinite (R_0AV) is 0.60%.
- Mineral matter: iron rich (pyrite/marcasite) and clay sized minerals finely disseminated throughout the matrix.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 010682

Contents:

	%
Isotropic bituminous matrix	88.0
Vitrinite - isotropic	4.2
- anisotropic	1.6
Inertinite	0.4
Mineral Matter - metallic	5.8
- other	-
	100%

Notes

- Isotropic bituminous matrix: contains abundant dispersed sub-micron sized metallic mineral (catalyst?).
  - Mesophase is present in the matrix.
  - Oil exudes from matrix.
  - The reflectance (R_0AV) of the matrix is 0.44%.
- Coal: comprises isotropic and anisotropic vitrinite and inertinite particles present in the bituminous matrix.
- The reflectance of the vitrinite is 0.60% (R_0AV).

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Appendix D-15

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue:151281

Contents:

	%
Isotropic bituminous matrix	94.7
Mesophase in matrix	-
Isotropic vitrinite	2.8
Isotropic inertinite	0.25
Anisotropic inertinite	0.25
Mineral Matter - metallic	2.0
other	-
	100%

Notes

- Isotropic bituminous matrix: very weakly reflecting, less vesicular than in most residues, has granular weakly reflecting rims 10-20 μm wide.
    - Vesicules are very small up to 10 μm diameter (produces a pitted appearance).
    - Mesophase spherules in the isotropic matrix.
    - The reflectance of isotropic matrix (R_0AV) is 0.28%.
- Coal particles: mostly isotropic, minor amounts are anisotropic.
- Oil present in granular areas of matrix.

Comments

Reflectance of matrix is low.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue:120582

Contents:

	%
Isotropic bituminous matrix	97.3
Isotropic vitrinite	1.7
Anisotropic vitrinite	0.3
Mineral Matter - metallic	0.7
	100%

Notes

- Isotropic bituminous matrix: comprises weakly reflecting, flourescent particles averaging 300 μm, which are slightly vesicular, and commonly have dark rims (20 μm).
- Oil exudes from matrix.
- Coal: very little present-comprises isotropic vitrinite particles up to <50 μm, minor amounts of anisotropic vitrinite.
- Inertinite: minor amounts.
- Mineral matter: iron rich, metallic, and fine clay sized particles which are concentrated in bituminous matrix.

Comments

Dark, weakly reflecting rims around some of the matrix particles suggest that the rims contain more hydrogen than the inner portions ? oil rich areas.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 120582 (toluene insoluble)

Contents:

	%
Remnants of isotropic bituminous matrix	93.9
Isotropic vitrinite	1.9
inertinite	1.0
Mineral Matter - metallic	3.2
- other	-
	100%

Notes

- Isotropic bituminous matrix: incompletely extracted, often centres of particles are concentrated and more highly reflecting like unextracted residue, particles up to 600 μm diameter, contain abundant sub-micron sized mineral particles and metallic mineral (catalyst).
- No oil exuding from matrix.
    - Some minor amounts of anisotropic, fine grained mosaic semicoke in matrix.
- Coal: small amounts of vitrinite and inertinite, particles <50 μm diameter, embedded in matrix.

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Appendix D-18

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 250682

Contents:

	%
Isotropic bituminous matrix	94.8
Mesophase	0.8
Vitrinite - isotropic	2.6
- anisotropic	1.0
Inertinite	0.4
Mineral Matter - metallic	0.4
- other	-
	100%

Notes

- Isotropic bituminous matrix: contains minor amounts of coal, mineral and mesophase.
- Much of the matrix is vesicular with vesicules most heavily concentrated near the perimeters but extending into interiors of particles.
- Mesophase spherules present in matrix range in size from 5 μm to 40 μm.
- The reflectance (R_0AV) of the matrix is 0.32%.
- Oil exudes from matrix.
- Coal: comprises vitrinite and inertinite particles; the vitrinite occurs in isotropic and anisotropic forms.
- The reflectance of the vitrinite (R_0AV) is 0.57%.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue:170582

Contents:

	%
Isotropic bituminous matrix	86.4
Isotropic vitrinite	6.0
inertinite	3.3
Mineral Matter - metallic	4.3
- other	-
	100%

Notes

- Bituminous matrix: isotropic, vesicular, dense or concentrated forms, weakly reflecting particles up to 550 μm, contains coaly particles and mineral matter.
- Coal: comprises vitrinite particles up to 50 μm diameter, and inertinite.
- Vitrinite reflectance (R_0AV) is 0.52%.
- Bituminous matrix: oil rich and fluoresces strongly.

Comments

Oil is light in colour (yellow-orange) and filters out of matrix, mixing with immersion oil. The reflectance of the vitrinite is similar to that in the feed mixture.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue:241181

Contents:

	%
Isotropic bituminous matrix	94.4
Isotropic vitrinite	2.0
inertinite	0.8
Mineral Matter - metallic	2.0
- other	0.8
	100%

Notes

- Isotropic bituminous matrix: highly concentrated, slightly to not vesicular, comprises particles up to 600 µm diameter, hosts coal particles and is peppered with finely disseminated mineral matter (metallic and clay-like).
- Oil exudes from matrix particles.
- Coal: isotropic vitrinite and inertinite, particles are 50-70 µm diameter and fewer than in many residues.
- Mineral: commonly occurs in clusters/aggregates.

Comments

Mineral component (iron rich, metallic) occurs in fairly high concentrations which may define the remains of dissolved coal particles - i.e. sizes and shapes similar to particles with surface catalyst present.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 190582

Contents:

	%
Isotropic bituminous matrix	86.4
Vitrinite - isotropic	6.6
- anisotropic	0.2
Inertinite	1.8
Mineral Matter - metallic	5.0
- other	-
	100%

Notes

- Bituminous matrix: isotropic, hosting coal and mineral matter.
  - Oil exudes from matrix.
  - The reflectance (R_0AV) of the matrix is 0.30%; the reflectance of the vitrinite is 0.61%
- Coal: vitrinite and inertinite particles; vitrinite occurs in both isotropic and anisotropic form.
- Mineral matter: metallic, sub-micron sized, dispersed throughout the matrix.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 140782

Contents:

	%
Isotropic bituminous matrix	89.4
Isotropic vitrinite	5.2
inertinite	0.2
Mineral Matter	5.2
	100%

Notes

- Bituminous matrix: isotropic, vesicular, dense, occurs as particulate matter up to 300-600 μm diameter hosts coal particles and mineral matter, commonly vesicular, fluoresces under blue/violet light.
- Oil exudes from matrix.
- Coal: particles comprise isotropic vitrinite and inertinite approximately 50 μm diameter.
- Mineral matter: iron rich (pyrite/marcasite) and clay sized minerals finely disseminated throughout the matrix.

Comments

Mineral matter - possibly catalyst

Similar to 170582 in composition and appearance.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 051181

Contents:

	%
Isotropic bituminous matrix	76.6
Mesophase	1.6
Medium grained mosaic-textured semicoke	3.6
Vitrinite - isotropic	8.6
- anisotropic	3.2
Inertinite	3.4
Mineral - metallic	3.0
- other	-
	100%

Notes

- Isotropic bituminous matrix: contains a high concentration of other material including vitrinite (isotropic and anisotropic), inertinite, mesophase, medium grained mosaic and mineral (mainly sub-micron sized, dispersed throughout matrix).
  - Some of the matrix particles are vesicular.
  - Oil exudes from matrix.
- The reflectance (% R_0AV) of the matrix is 0.28%.
- Coal: the vitrinite particles are both isotropic and anisotropic.
- The reflectance of the vitrinite, $R_0AV = 0.48\%$.

Comments

The reflectance of the vitrinite is slightly less than that of the feed mixture.

PETROGRAPHIC ANALYSIS OF LIQUEFACTION RESIDUE

Residue: 190282

Contents:

	%
Isotropic bituminous matrix	94.4
Vitrinite	3.6
Inertinite	0.8
Mineral Matter - metallic	1.2
- other	-
	100%

Notes

- Bituminous matrix: isotropic and occurs as particles up to 600 µm diameter, many of the particles contain vesicules and some have slightly higher reflecting rims (<20 µm).
    - Some mesophase and fine-medium grained anisotropic material are present in the matrix in minor amounts.
    - Oil exudes from matrix.
    - The reflectance (R_0AV) of the matrix is 0.30%; the reflectance of the vitrinite is 0.60%.
- Coal (vitrinite and inertinite) particles are imbedded in the matrix. As no coal was present in the initial charge, the coal particles are contaminants. They occur within the bituminous matrix and therefore, it is unlikely that they were introduced during preparation of samples for petrographic analysis.

Comments

Small particles of coal present - contamination?

APPENDIX E

Trace element analyses of coal-bitumen coprocessing feedstocks and residues by SEM-EDS

Appendix E-1

Sample No.	Component Identification	Weight percent of major elements (0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #0	Vitrinite	-	-	7.7	7.2	25.4	4.7	-	-	1.4	53.5	
	Structured vitrinite	-	-	8.4	7.1	24.9	5.4	-	-	1.1	53.1	
	Inertinite	-	-	7.9	6.8	25.4	6.0	-	-	0.9	53.1	
	Mineral matter	-	-	9.1	11.9	19.6	5.5	-	-	2.3	51.6	
	Mineral matter	-	-	6.0	11.3	23.3	5.0	-	-	0.9	53.4	
	Mineral matter	-	-	5.5	17.7	20.5	-	-	-	0.5	55.8	

*Cl from mounting resin

Table E-1: Quantitative elemental analyses of Forestburg coal used by Raylo Chemicals Ltd for coal/bitumen coprocessing experiments

Sample No.	Component Identification	Weight percent of major elements (±0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #1	Structured vitrinite	-	-	6.2	8.0	25.7	5.7	-	-	1.0	53.4	
	Groundmass vitrinite	-	-	7.0	8.4	24.9	5.4	-	-	1.0	53.3	
	Inertinite	-	-	8.4	7.3	24.9	6.5	-	-	-	53.0	
	Inertinite	-	-	7.9	6.8	25.9	5.6	-	-	0.3	53.6	
	Mineral matter	-	-	7.4	4.9	14.1	1.2	-	-	14.3	41.5	Cu = 16.7
	Mineral matter	-	-	7.5	9.7	25.9	0.3	-	-	-	56.6	
	Mineral matter (large area scan)	-	-	7.4	7.4	26.0	4.9	-	-	0.2	54.1	

*Cl from mounting resin

Table E-2: Quantitative elemental analyses of residues from Forestburg coal heated in anthracene oil, Raylo Chemicals Ltd.

Appendix E-3

Sample No.	Component Identification	Weight percent of major elements (±0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #2	Coarse-grained anisotropic bitumen	-	-	-	5.5	32.1	7.9	-	-	-	54.4	
	Coarse-flow anisotropic bitumen	-	-	-	5.2	32.0	8.8	-	-	-	53.9	
	Mesophase + isotropic bitumen	-	-	4.4	5.3	29.5	6.8	-	-	-	54.1	

*Cl from mounting resin

Table E-3: Quantitative elemental analyses of componments in bitumen coke, Raylo Chemicals Ltd.

Appendix E-4

Sample No.	Component Identification	Weight percent of major elements (±0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #3	Isotropic vitrinite	-	-	7.7	7.2	25.4	4.7	-	-	1.4	53.5	
	Fine-grained anisotropic vitrinite	-	-	9.8	8.4	21.2	10.6	-	-	-	50.0	
	Fine-grained anisotropic vitrinite	-	-	8.9	9.8	19.8	12.3	-	-	-	49.0	
	Medium-grained anisotropic vitrinite	-	-	9.5	8.9	20.3	12.0	-	-	0.3	49.0	
	Medium-grained anisotropic vitrinite	-	-	8.9	9.1	20.6	12.2	-	-	-	49.2	
	Coarse-grained anisotropic vitrinite	-	-	8.8	8.6	21.2	12.0	-	-	-	49.4	
	Mesophase	-	-	9.5	8.9	20.1	12.8	-	-	-	48.7	

*Cl from mounting resin

Table E-4: Quantitative elemental analyses of components in coal coke, Raylo Chemicals Ltd.

Appendix E-5

Sample No.	Component Identification	Weight percent of major elements (±0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #4	Fine-grained anisotropic vitrinite	-	-	9.1	8.4	21.5	11.4	-	-	-	49.7	These analyses are on coal derived material
	Fine-grained anisotropic vitrinite	-	-	8.5	9.1	25.9	-	-	-	-	56.6	
	Fine-grained anisotropic vitrinite	-	-	11.5	-	31.4	-	-	-	-	57.2	
	Isotropic vitrinite	-	-	9.0	6.2	26.5	-	-	-	2.9	55.5	

*Cl from mounting resin

Table E-5: Quantitative elemental analyses of coal/bitumen liquefaction residue, Raylo Chemicals Ltd.

Appendix E-6

Sample No.	Component Identification	Weight percent of major elements (± 0.4 (average))										Remarks
		Na	Mg	Al	Si	S	*Cl	K	Ca	Fe	C,H,N,O	
C-B-Co #4	Coarse-grained anisotropic bitumen	-	-	4.5	2.7	34.4	-	-	-	-	58.5	These analyses are on bitumen derived material
	Coarse-flow anisotropic bitumen	-	-	5.6	3.4	32.9	-	-	-	-	58.1	
	Coarse-flow anisotropic bitumen	-	-	7.1	-	34.7	-	-	-	-	58.2	
	Coarse-grained anisotropic bitumen	-	-	7.1	-	34.7	-	-	-	-	58.2	

*Cl from mounting resin

Table E-6: Quantitative elemental analyses of coal/bitumen residue, Raylo Chemicals Ltd.

POOR

QUALITY

ORIGINAL